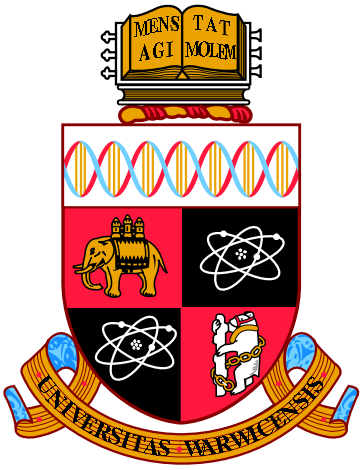

Diffuse Interface Models of Soluble Surfactants in Two-Phase Fluid Flows

by

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Lastly, I express my gratitude to my family and friends for their continuing support and encouragement.

Declarations

I declare that this thesis contains entirely my own research, conducted under the supervision of Björn Stinner and Charles Elliott, except where otherwise stated. It has not been submitted for a degree at any other university. It has not been submitted for award at any other institution or for any other qualification.

The material in Chapters 2, 3 and 4 are taken from a paper co-authored with Harald Garcke and Björn Stinner and published in Communications in Mathematical Science [Garcke et al., 2014]. The 2D simulations presented in Section 4.2.2 and the idea of Model C are due to Björn Stinner, while the reformulation of the surfactant equations, energy inequality for the phase field model, alternate asymptotic analysis for Model A and the asymptotics of Model B using the flux expansion are due to Harald Garcke.

The material in Chapter 5 is joint work with Helmut Abels and Björn Stinner.

Abstract

Surface active agents (surfactants) reduce the surface tension of fluid interfaces and, via surface tension gradients, can lead to tangential forces resulting in the Marangoni effect. Biological systems take advantage of their impact on fluids with interfaces, but surfactants are also important for industrial applications such as processes of emulsification or mixing.

Surfactants can be soluble in at least one of the fluid phases and the exchange of surfactants between the bulk phases and the fluid interfaces is governed by the process of adsorption and desorption. One can compute the interfacial surfactant density from the bulk surfactant density by assuming that the interface is in equilibrium with the adjacent bulk phase and imposing a closure relation (known as adsorption isotherm) between the two quantities. The assumption (known as instantaneous adsorption) is valid when the process of adsorption to the interface is fast compared to the kinetics in the bulk phases. However, it is not valid in the context of ionic surfactant systems, or when the diffusion is not limited to a thin layer.

In this thesis, we derive two types of mathematical models for two-phase flow with a soluble surfactant that can account for both instantaneous and non-instantaneous adsorption. The first type is a sharp interface model, in which the interface is modelled by moving hypersurfaces. While the second type is a phase field model, in which the interface is a region of small, nonzero thickness where there is some microscopic mixing of the two fluids. Both types of models are shown to satisfy energy inequalities which guarantee thermodynamical consistency.

Via a formal asymptotic analysis, we show the phase field models are related to sharp interface models in the limit that the interfacial width tends to zero. Flexibility with respect to the choice of bulk and surface free energies allows us to realise various isotherms and relations of state between surface tension and surfactant. We present some numerical simulations to support the asymptotic analysis and display the effectiveness of the our approach.

As a first step towards an analysis of our models, we consider sharp interface and phase field models for soluble surfactants in a static situation. The surfactant equations become a linear elliptic coupled bulk-surface partial differential equation, and our main result is the rigorous convergence of the weak solution of the phase field models to the weak solution of the sharp interface models.

Chapter 1

Introduction

1.1 Surfactants in emulsification

Emulsification is an important industrial process that involves mixing two or more fluids that normally are unmixable. More precisely, in the process of emulsification, it is desirable to have stable dispersions of one fluid in another (see Figure 1.1). Common examples of emulsions are milk, fire extinguishers and hand cream. The mixture is thermodynamically unstable and will progressively revert back to their unmixed states over time. Surface active agents (or surfactants) are often added to increase the stability of the mixture and hence there is great interest, especially in industrial applications, to understand the influence of surfactants on the dynamics of multi-fluid systems.

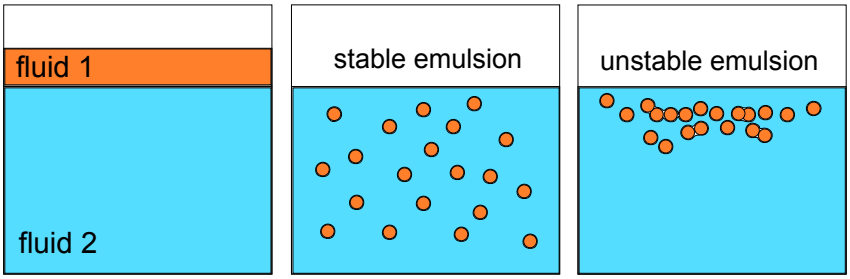


Figure 1.1: Two immiscible fluids that are not yet emulsified. If the surface tension between the fluids are reduced, one might see that fluid 1 enters a dispersed phase and is dispersed into fluid 2. The emulsion is termed stable if one fluid is fully dispersed in the other. Otherwise, an unstable emulsion will progressively separate. Surfactants are often used to reduce the surface tension between the fluids, and thus stabilising the emulsions.

Surface tension forces play a significant role in emulsification. Interfacial

tension between the two fluids exist due to the immisicibility of the fluids and emulsification takes place when the tension between the two fluids is low enough. By adhering to the interfaces and creating a buffer zone, surfactants reduce the surface tension of the interfaces, which permits stability of small droplets of one fluid suspended in a bulk of the other fluid.

Moreover, the local differences in surface tension can cause surfactants to diffuse along the interface, a phenomenon known as the Marangoni effect. This in turn changes the shape of the interface and leads to more diffusion of the surfactants. This complex coupling between surfactants and the fluids is at the heart of many industrial processes involved in emulsification.

Surfactants can be broadly classified into soluble and insoluble surfactants. While soluble surfactants can exist in the bulk fluid phases and on the interface, surfactants that are insoluble will only exist within the interface, and so when introduced to a multi-fluid system, they will migrate towards the interface by the process of adsorption. Much previous work have been done to understand the process of adsorption and to postulate a model for surfactant dynamics.

One of the simplest models for adsorption dynamics is the model of Ward and Tordai [1946]. Consider a semi-infinite region $\Omega := (0, \infty)$ with interface $\Gamma = \{0\}$. Let the bulk surfactant concentration in Ω be given by c and the interfacial surfactant concentration be given by c^Γ. We also define the sub-layer or the sub-surface to be the bulk region immediately next to the interface. On the assumption that equilibrium between the sub-layer and the interface is established instantaneously (this is known as diffusion controlled adsorption or instantaneous adsorption [Diamant and Andelman, 1996]), the model of Ward and Tordai [1946] reads as:

$$\begin{aligned} \frac{\partial c}{\partial t} &= D\frac{\partial^2 c}{\partial x^2} \text{ for } x > 0, t > 0, \\ \frac{\partial c^\Gamma}{\partial t} &= D\frac{\partial c}{\partial x} \text{ at } x = 0, t > 0, \end{aligned}$$

with initial and boundary conditions

$$\lim_{x\to\infty} c(x,t) = c_b \text{ for } t > 0,\ c(x,0) = c_b,\ c^\Gamma(0) = 0.$$

In their work, Ward and Tordai derived an expression for c^Γ:

$$c^\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left(c_b\sqrt{t} - \int_0^{\sqrt{t}} c(0, t-\tau)d\sqrt{\tau}\right),$$

where $c(0,t)$ is the concentration in the sub-layer. Since the sub-layer and the interface are in equilibrium, we can impose a relation between $c(0,t)$ and $c^\Gamma(t)$:

$$c(0,t) = g(c^\Gamma(t)),$$

for some function g. This functional relation is often termed adsorption isotherm, which relates the concentration in the sub-layer with the concentration on the interface. More importantly, the Ward–Tordai equation becomes:

$$c^\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left(c_b\sqrt{t} - \int_0^{\sqrt{t}} g(c^\Gamma(t-\tau))d\sqrt{\tau}\right),$$

and a Newton method can be employed to solve for $c^\Gamma(t)$ (see [Li et al., 2010]).

Several hypotheses have been proposed regarding the form for the adsorption isotherm, leading to the development of forms for g. Table 2.1 displays six of the isotherms used in the literature, those of Henry, Langmuir, Volmer, van der Waals, Freundlich, and Frumkin (see also [Eastoe and Dalton, 2000; Kralchevsky et al., 1999, 2008]), along with the functional forms for the interfacial free energy density $\gamma(c^\Gamma)$, the bulk free energy density $G(c)$ and the surface tension $\sigma(c^\Gamma)$.

We remark that the central assumption to the Ward–Tordai equation is that the sub-layer and the interface are in thermodynamical equilibrium at all times, i.e. the process of adsorption is fast compared to the kinetics in the bulk regions. This corresponds to the case of diffusion-limited adsorption studied in Diamant and Andelman [1996]. However, instantaneous adsorption is not valid in the context of ionic surfactant systems [Diamant and Andelman, 1996] or when the diffusion is not limited to a thin layer [Coutelieris, 2002; Coutelieris et al., 2003, 2005]. In these situations, we will not have a closure relation for $c(0,t)$ and $c^\Gamma(t)$. Therefore, we would like to develop models that are able to account for both instantaneous and non-instantaneous adsorption.

1.2 Sharp interface models

Two-phase flow with surfactant is classically modelled with moving hypersurfaces describing the interfaces separating the two fluids. The first contribution of this thesis is the derivation of a general sharp interface model of soluble surfactants in two-phase flow in an isothermal setting. This is done in Chapter 2. Our model is able to cover both instantaneous and non-instantaneous adsorption and is general enough to allow for a wide range of isotherm relations.

Let Ω denote an open bounded domain in $\mathbb{R}^n$ containing two fluids of different mass densities. We denote by $\Omega^{(1)}(t)$, $\Omega^{(2)}(t)$ the domains of the fluids which are separated by an interface $\Gamma(t)$. The sharp interface model is given as:

$$\nabla \cdot \boldsymbol{v} = 0, \text{ in } \Omega^{(i)}(t), \tag{1.2.1}$$

$$\partial_t(\overline{\rho}^{(i)}\boldsymbol{v}) + \nabla \cdot (\overline{\rho}^{(i)}\boldsymbol{v} \otimes \boldsymbol{v}) = \nabla \cdot \left(-p\boldsymbol{I} + 2\eta^{(i)}D(\boldsymbol{v})\right), \text{ in } \Omega^{(i)}(t), \tag{1.2.2}$$

$$\partial_t^\bullet c^{(i)} = \nabla \cdot (M_c^{(i)} \nabla G_i'(c^{(i)})), \text{ in } \Omega^{(i)}(t), \tag{1.2.3}$$

$$[\boldsymbol{v}]_1^2 = 0, \quad \boldsymbol{v} \cdot \boldsymbol{\nu} = u_\Gamma, \text{ on } \Gamma(t), \tag{1.2.4}$$

$$[p\boldsymbol{I} - 2\eta^{(i)}D(\boldsymbol{v})]_1^2\boldsymbol{\nu} = \sigma(c^\Gamma)\kappa\boldsymbol{\nu} + \nabla_\Gamma\sigma(c^\Gamma), \text{ on } \Gamma(t), \tag{1.2.5}$$

$$\partial_t^\bullet c^\Gamma + c^\Gamma \nabla_\Gamma \cdot \boldsymbol{v} - \nabla_\Gamma \cdot (M_\Gamma \nabla_\Gamma \gamma'(c^\Gamma)) = [M_c^{(i)} \nabla G_i'(c^{(i)})]_1^2 \boldsymbol{\nu}, \text{ on } \Gamma(t), \tag{1.2.6}$$

$$\alpha^{(i)}(-1)^i M_c^{(i)} \nabla G_i'(c^{(i)}) \cdot \boldsymbol{\nu} = -(\gamma'(c^\Gamma) - G_i'(c^{(i)})), \text{ on } \Gamma(t). \tag{1.2.7}$$

Here $\boldsymbol{v}$ denotes the fluid velocity, $\overline{\rho}^{(i)}$ is the constant mass density for fluid i, $\eta^{(i)}$ is the viscosity of fluid i, $D(\boldsymbol{v}) = \frac{1}{2}(\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^\perp)$ is the rate of deformation tensor, p is the pressure, $\boldsymbol{I}$ is the identity tensor, $\partial_t^\bullet(\cdot) = \partial_t(\cdot) + \boldsymbol{v}\cdot\nabla(\cdot)$ is the material derivative, $c^{(i)}$ is the bulk density of surfactant in fluid i, $M_c^{(i)}$ is the mobility of surfactants in fluid i, $G_i(c^{(i)})$ is the bulk free energy density associated to the bulk surfactant in fluid i. On the interface, $[\cdot]_1^2$ denotes the jump of the quantity in brackets across Γ from $\Omega^{(1)}$ to $\Omega^{(2)}$, u_Γ is the normal velocity, $\boldsymbol{\nu}$ is the unit normal on Γ pointing into $\Omega^{(2)}$, c^Γ is the interfacial surfactant density, $\sigma(c^\Gamma)$ is the density dependent surface tension, κ is the mean curvature of Γ, ∇_Γ is the surface gradient operator, $\nabla_\Gamma\cdot$ is the surface divergence, M_Γ is the mobility of the interfacial surfactants, $\gamma(c^\Gamma)$ is the free energy density associated to the interfacial surfactant, and $\alpha^{(i)} \geq 0$ is a kinetic factor that relates to the speed of adsorption. The above model satisfies the second law of thermodynamics in an isothermal situation in the form of an energy dissipation inequality.

Equations (1.2.1) and (1.2.2) are the classical incompressibility condition and momentum equation, respectively. The mass balance equation for bulk surfactants is given by (1.2.3). Equation (1.2.4) states that the interface is transported with the flow and that not only the normal components but also the tangential components of the velocity field match up. The force balance on the interface (1.2.5) relates the jump in the stress tensor across the interface to the surface tension force and the Marangoni force at the interface. The mass balance of the interfacial surfactants is given by (1.2.6), and the closure condition (1.2.7) tells us whether adsorption is instantaneous ($\alpha^{(i)} = 0$, an isotherm is obtained) or non-instantaneous ($\alpha^{(i)} > 0$, the mass flux into the interface is proportional to the difference in chemical potentials).

In this model, the surface tension $\sigma : \mathbb{R}_+ \to \mathbb{R}_+$, $\mathbb{R}_+ := [0, \infty)$, is a (usually decreasing) function of the surfactant density c^Γ. The phenomenon known as Marangoni effect, where tangential stress at the phase boundary leads to flows along the interface, is incorporated into the model via the surface gradient of σ in the momentum jump free boundary condition (1.2.5).

We remark that if the setting is non-isothermal, the Marangoni effect can be caused by temperature gradients in the absence of surfactants. In this case, we will have one temperature field $\theta^{(i)}$, $i = 1, 2$, for each of the phases and they satisfy

$$\begin{aligned} \partial_t \theta^{(i)} + \boldsymbol{v} \cdot \nabla \theta^{(i)} &= \kappa^{(i)} \Delta \theta^{(i)}, \text{ in } \Omega^{(i)}(t), \\ [\theta^{(i)}]_1^2 = 0, \quad [\kappa^{(i)} \nabla \theta^{(i)}]_1^2 \boldsymbol{\nu} &= 0, \text{ on } \Gamma(t), \end{aligned}$$

where $\kappa^{(i)}$ is the thermal conductivity of fluid i. The surface tension σ is now a function (typically linear and decreasing) of the interface temperature θ, defined as the average $\theta = \frac{1}{2}(\theta^{(1)} + \theta^{(2)})|_{\Gamma(t)}$. The model of Rayleigh–Marangoni–Bénard convection in two-phase flow consists of the above equations involving the temperature fields, (1.2.1), (1.2.2), (1.2.4), and (1.2.5) with $\sigma(\theta)$ instead of $\sigma(c^\Gamma)$.

The model studied in Bothe, Prüss, and Simonett [2005]; Bothe and Prüss [2010] bears the most resemblance to the above model (1.2.1) – (1.2.7), where the setting of these papers is the diffusion-limited regime with a surfactant which is soluble in one phase only and (1.2.7) is replaced by the relation

$$\gamma'(c^\Gamma) = G'(c) \quad \Longleftrightarrow \quad c^\Gamma = g(c) := (\gamma')^{-1}(G'(c)), \tag{1.2.8}$$

in which g plays the role of the equilibrium isotherm and G is the bulk free energy of the phase in which the surfactant is soluble. Our approach is based on a free energy formulation, originated from Diamant and Andelman [1996]; Diamant et al. [2001], where we gain access to equilibrium isotherms by setting $\alpha^{(i)} = 0$ and choosing suitable functions for γ and G_i. Furthermore, for positive values of $\alpha^{(i)}$ we are able to include the dynamics of non-equilibrium adsorption.

Regarding the analysis of the sharp interface models, we mention the short time existence results for one-phase Navier–Stokes equation with a free surface in Solonnikov [1977, 1986]; Allain [1987]; Beale [1980]; Tani [1996], and the long time existence results in Beale [1984]; Tani and Tanaka [1995]. For the one-phase Rayleigh–Marangoni–Bénard convection model, unique solvability for the stationary case is shown in Aberge and Dupaix [1996], while, for the non-stationary problem, local in time unique solvability in Sobolev spaces and in Hölder spaces are shown in Wagner [1999] and Lagunova [1993], respectively. For isothermal two-phase flows,

the most general existence result is the global in time existence of measure-valued varifold solutions of Abels [2007]. We also mention the results of Tanaka [1993]; Giga and Takahasi [1994]; Nouri and Poupaud [1995]; Denisova [2000]; Prüss and Simonett [2010]; Xu and Zhang [2010]. For the two-phase Rayleigh–Marangoni–Bénard convection model, local in time existence has been proved in Tanaka [1995].

To the author's best knowledge, the only existence result regarding classical models of soluble surfactants in two-phase flow is that of Bothe, Prüss, and Simonett [2005], where short time existence of classical solutions to a one-sided version of $(1.2.1) - (1.2.6), (1.2.8)$ for special configurations is shown. A subsequent analysis of the stability of equilibria can be found in Bothe and Prüss [2010].

1.3 Phase field models

The governing equations $(1.2.1) - (1.2.7)$ form a free boundary problem. The phase boundary $\Gamma(t)$ is unknown a priori and hence must be computed as part of the solution. Much work have been dedicated to explicitly tracking and capturing the interface using various numerical methods. Popular methods include level set methods [Xu et al., 2006; Gross and Reusken, 2011; Xu et al., 2014], front-tracking methods [Muradoglu and Tryggvason, 2008; Lai et al., 2008; Khatri and Tornberg, 2011], volume-of-fluid methods [James and Lowengrub, 2004; Alke and Bothe, 2009; Renardy et al., 2002] and arbitrary Lagrangian–Eulerian methods [Yon and Pozrikidis, 1998; Yang and James, 2009; Ganesan and Tobiska, 2009; Barrett et al., 2013].

Despite significant advances in the modelling and computation of two-phase flows, the sharp interface description breaks down when topological changes of the interface occur. Phenomena such as breakup of fluid droplets, reconnection of fluid interfaces, pinching, coalescence, cusp formation, and tip-streaming driven by Marangoni forces [Fernandez and Homsy, 2004; Krechetnikov and Homsy, 2004a,b] involve changes in the topology of the interface. At such an event, the fluid interface cannot be represented by a hypersurface and so the sharp interface equations are no longer valid. Numerically, complications also arise when the shape of the interface becomes complicated or exhibits self-intersections.

Current numerical methods, such as front-tracking and front-capturing, will have to use ad-hoc procedures to deal with these singular events during computation. In a front-tracking method, the fluid interface is explicitly represented in the form of Lagrangian markers and additional computational elements are introduced to keep track of the interface. When a topological transition event approaches, a decision has to be made whether to allow such a transition to occur and if so when and

how to perform an interfacial reconnection [Unverdi and Tryggvason, 1992]. On the other hand, in a front-capturing method, the interface is embedded as a level set of a function defined throughout the computational domain. This formulation allows the numerical method to transition through a topological singularity without any additional intervention, but re-initialisation of the level set might be necessary for mass conservation or to maintain the signed distance property (see [Chang et al., 1996; Sussman et al., 1994]).

These difficulties have led to the development of diffuse interface (or phase field) models to provide an alternative description of fluid/fluid interfaces. At the core of these models, it is assumed that there is some microscale mixing of the macroscopically immiscible fluids and the sharp interface is replaced by an interfacial layer of finite width. Within this region the two fluids are mixed and the model has to account for certain mixing energies. An order parameter is introduced to distinguish between the fluids within the interfacial layer, where it takes distinct constant values in each of the bulk regions and varies smoothly across the narrow interfacial layer (see Figure 1.2). The original sharp interface can then be represented as the zero level set of the order parameter, which draws on ideas of the front-capturing method, thus allowing different level sets to exhibit different topologies. We mention the work of Lowengrub et al. [1999]; Lowengrub and Truskinovsky [1998] on the investigation of phase field models near topological transitions in the context of two-phase flows.

We remark that, in contrast to the front-capturing method where the interface is represented as a level set of an artificial function, the order parameter in the phase field model can have physical meaning. For example, one can choose the order parameter to be the difference in volume fraction, the difference in mass concentration or the density difference (see [Abels et al., 2011; Lowengrub and Truskinovsky, 1998]).

1.3.1 Choice of potentials

At the centre of the phase field models lies the Ginzburg–Landau energy density:

$$\mathcal{E}_{GL}(\varphi, \nabla\varphi) := \frac{\varepsilon}{2}\,|\nabla\varphi|^2 + \frac{1}{\varepsilon}W(\varphi), \tag{1.3.1}$$

where φ is the order parameter, ε is a measure of interfacial thickness and $W(\varphi)$ is a potential with equal minima at $\varphi = \pm 1$ and symmetric about $\varphi = 0$. In most applications, W is chosen to be a potential of double-well or double-obstacle type [Blowey and Elliott, 1991, 1993]. For example, one can choose $W(\varphi) = \frac{1}{4}(1-\varphi^2)^2$

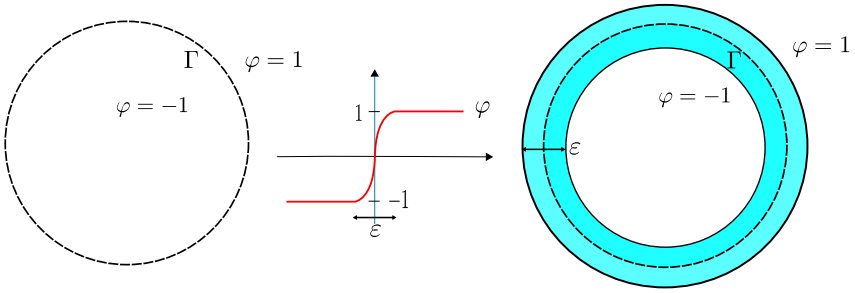


Figure 1.2: The order parameter φ contains information about the location of the phases. If $\Omega^{(1)}$ is the region where $\varphi = -1$ and $\Omega^{(2)}$ is the region where $\varphi = +1$, then in the sharp interface model, φ jumps across the interface. The phase field methodology replaces the original hypersurface Γ with an interfacial layer of thickness ε and allows φ to transition smoothly from one phase to the other.

for a potential of double-well type or

$$W(\varphi) = \frac{1}{2}(1-\varphi^2) + I_{[-1,1]}(\varphi), \quad I_{[-1,1]}(\varphi) = \begin{cases} 0, & \text{if } |\varphi| \leq 1, \\ \infty, & \text{else,} \end{cases}$$

for a potential of double-obstacle type (see Figure 1.3). The potential term $W(\varphi)$ prefers the order parameter φ in its minima at ± 1 and the gradient term $|\nabla\varphi|^2$ penalises large jumps in gradient. This leads to the development of bulk regions where φ is close to ± 1 which are separated by a narrow interfacial layer.

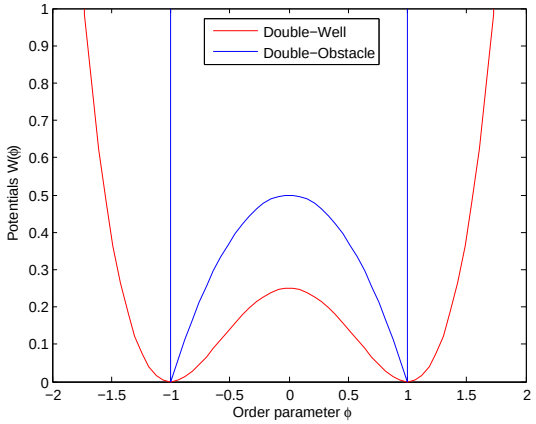


Figure 1.3: The double well and double obstacle potentials. Notice that the double obstacle potential penalises heavily if $\varphi \notin [-1, 1]$.

Often, a double-well potential is used for the derivation of phase field models due to its smoothness properties. However, an inherent disadvantage of the double-

well potential is that the order parameter φ may not strictly lie in the interval $[-1, 1]$. For order parameters that have physical meaning, such as the difference in volume fraction between two fluids, the physical interpretation of $\varphi < -1$ or $\varphi > 1$ is unclear. On the other hand, the penalty term $I_{[-1,1]}(\varphi)$ of the double-obstacle potential confines φ to lie in the interval $[-1, 1]$, and so there is no ambiguity in identifying φ with a physical parameter. A drawback of using a double-obstacle potential is that the resulting model equations are replaced by variational inequalities, and subsequent analysis of the models are more complicated than those with a double-well potential. We refer to Chen and Elliott [1994] for a discussion involving the two choice of potentials.

1.3.2 Phase field models for two-phase flow

The review Anderson et al. [1998] provides an overview on diffuse interface methods in the context of fluid flows. In Gurtin, Polignone, and Viñals [1996]; Hohenberg and Halperin [1977] it was already proposed to combine a Cahn-Hilliard equation for distinguishing the two phases with a Navier-Stokes system. An additional term was included in the momentum equation to model the surface contributions to forces. In the case of different densities, Lowengrub and Truskinovsky [1998] derived quasi-incompressible models, where the fluid velocity is not divergence free. On the other hand, Ding, Spelt, and Shu [2007] has derived a diffuse interface model for two-phase flow with different densities and with solenoidal fluid velocities. But it is not known whether this model is thermodynamically consistent. Most recently, a phase field model for non-matched densities and divergence-free velocity that satisfies local and global energy inequalities has been derived by Abels, Garcke, and Grün [2011].

For matched densities, we mention the work of Abels [2009b]; Boyer [1999]; Liu and Shen [2003] on the existence of weak solutions to the phase field model for two-phase flow. For general densities, the existence of weak solutions to the model of Abels, Garcke, and Grün [2011] are shown in Abels, Depner, and Garcke [2013a,b] using a time discretisation and in [Grün, 2013] using a full discretisation. Existence of weak solutions to variants of the model of Lowengrub and Truskinovsky [1998] are shown in Abels [2009a, 2012]. We remark that for a different phase field model for fluids with non-matched densities, Boyer [2001] proved local existence of strong solutions and global existence of weak solutions if the densities of the fluids are sufficiently close.

1.3.3 Phase field models for surfactants in two-phase flow

Generalising the model of Abels, Garcke, and Grün [2011], the second contribution of this thesis is the derivation of three diffuse interface models for soluble surfactants in two-phase flow. This is done in Chapter 3. For the case of non-instantaneous adsorption ($\alpha^{(i)} > 0$), we will derive the following model (denoted Model A):

$$\nabla \cdot \boldsymbol{v} = 0, \tag{1.3.2}$$

$$\begin{aligned}\partial_t(\rho\boldsymbol{v}) + \nabla\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{v}) &= \nabla\cdot\Big(-p\boldsymbol{I} + 2\eta(\varphi)D(\boldsymbol{v}) + \boldsymbol{v}\otimes\tfrac{\overline{\rho}^{(2)}-\overline{\rho}^{(1)}}{2}m(\varphi)\nabla\mu\Big) \\ &\quad + \nabla\cdot\big(\sigma(c^\Gamma)(\delta(\varphi,\nabla\varphi)\boldsymbol{I} - \mathcal{W}\varepsilon\nabla\varphi\otimes\nabla\varphi)\big),\end{aligned} \tag{1.3.3}$$

$$\partial_t^\bullet\varphi = \nabla\cdot(m(\varphi)\nabla\mu), \tag{1.3.4}$$

$$\begin{aligned}\mu &= -\nabla\cdot(\mathcal{W}\varepsilon\sigma(c^\Gamma)\nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\sigma(c^\Gamma)W'(\varphi) \\ &\quad + \sum_{i=1,2}\xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)}),\end{aligned} \tag{1.3.5}$$

$$\begin{aligned}\partial_t^\bullet(\xi_i(\varphi)c^{(i)}) &= \nabla\cdot(M_c^{(i)}(c^{(i)})\xi_i(\varphi)\nabla G_i'(c^{(i)})) \\ &\quad + \frac{1}{\alpha^{(i)}}\delta(\varphi,\nabla\varphi)(\gamma'(c^\Gamma) - G_i'(c^{(i)})), \quad i=1,2,\end{aligned} \tag{1.3.6}$$

$$\begin{aligned}\partial_t^\bullet(\delta(\varphi,\nabla\varphi)c^\Gamma) &= \nabla\cdot\big(M_\Gamma(c^\Gamma)\delta(\varphi,\nabla\varphi)\nabla\gamma'(c^\Gamma)\big) \\ &\quad - \delta(\varphi,\nabla\varphi)\sum_{i=1,2}\frac{1}{\alpha^{(i)}}(\gamma'(c^\Gamma) - G_i'(c^{(i)})).\end{aligned} \tag{1.3.7}$$

Here ε is a length scale associated with the interfacial width, φ is the order parameter that distinguishes the two bulk phases. In fact φ takes values close to ± 1 in the two phases and rapidly changes from -1 to 1 in an interfacial layer. The functions $\xi_i(\varphi)$ and $\delta(\varphi,\nabla\varphi)$ act as regularisations to the Dirac measures of $\Omega^{(i)}$ and Γ, respectively, while $\mathcal{W}$ is a constant related to $\delta(\varphi,\nabla\varphi)$. Equations (1.3.2) and (1.3.3) are the incompressibility condition and the phase field momentum equations, respectively. Equation (1.3.4) together with (1.3.5) governs how the order parameter evolves and equations (1.3.6) and (1.3.7) are the bulk and interfacial surfactant equations, respectively.

We derive two additional models for instantaneous adsorption ($\alpha^{(i)} = 0$): Model B models the case where there is instantaneous adsorption in $\Omega^{(2)}$ and non-instantaneous adsorption in $\Omega^{(1)}$. It consists of (1.3.2) – (1.3.5) and replaces the

bulk and interface surfactant equations (1.3.6), (1.3.7) with

$$\partial_t^\bullet(\xi_1 c^{(1)}) = \nabla \cdot (M_c^{(1)}(c^{(1)})\xi_1 \nabla G_1'(c^{(1)})) + \frac{1}{\alpha^{(1)}}\delta(G_2'(c^{(2)}) - G_1'(c^{(1)})), \tag{1.3.8}$$

$$\begin{aligned}\partial_t^\bullet(\xi_2 c^{(2)} + \delta g(c^{(2)})) = \nabla \cdot ((M_c^{(2)}\xi_2 + M_\Gamma(g(c^{(2)})))\delta \nabla G_2'(c^{(2)})) \\ - \frac{1}{\alpha^{(1)}}\delta(G_2'(c^{(2)}) - G_1'(c^{(1)})),\end{aligned} \tag{1.3.9}$$

where $g(c^{(2)})$ is the adsorption relation as in (1.2.8).

The case where there is instantaneous adsorption in both bulk phases is covered by Model C, which consists of (1.3.2) – (1.3.5) and

$$\begin{aligned}\partial_t^\bullet(\xi_1 c^{(1)}(q) + \xi_2 c^{(2)}(q) + \delta c^\Gamma(q)) - \sum_{i=1,2} \nabla \cdot (M_i(c^{(i)}(q))\xi_i \nabla q) \\ - \nabla \cdot (M_\Gamma(c^\Gamma(q))\delta \nabla q) = 0.\end{aligned} \tag{1.3.10}$$

Here, q denotes a chemical potential where, as will be discussed in Chapter 3, we can express the surfactant densities as functions of q.

The Model A is related to the approach in Teigen et al. [2009]. We modify the approach of Teigen et al. [2009] in such a way that an energy inequality is valid and such that we recover the isotherm relations for adsorption phenomena in the limit of instantaneous adsorption. We deepen the asymptotic analysis in that it works with the original equation for the surface quantity and does not require the assumption of extending the surface quantity continuously in the normal direction.

We remark that Model B is more intuitive at considering instantaneous adsorption, since the relation (1.2.8) can be seen directly in surfactant equations. As we can express c^Γ as a function of $c^{(2)}$, we add the equations for $c^{(2)}$ and $g(c^{(2)})$ to obtain (1.3.9). If we also consider instantaneous adsorption in $\Omega^{(1)}$, then this would lead to the relation

$$G_1'(c^{(1)}) = G_2'(c^{(2)}) = \gamma'(c^\Gamma). \tag{1.3.11}$$

We may choose to express $c^{(1)}$ and c^Γ as functions of $c^{(2)}$ and upon adding (1.3.8) and (1.3.9) with (1.3.11) in mind, we arrive at a single equation similar to (1.3.10). However, since $c^{(2)}$ is not determined everywhere in Ω (due to the presence of ξ_2), Model C is developed based on expressing the surfactant densities in terms of a common chemical potential q which is defined everywhere in Ω (see Section 3.4 for more details).

1.3.4 Phase field models with two order parameters

Phase field models of surfactant adsorption that utilise the free energy approach of Diamant and Andelman [1996]; Diamant, Ariel, and Andelman [2001] can be traced back to the models of Theissen and Gompper [1999]; Teramoto and Yonezawa [2001]; van der Sman and van der Graaf [2006]. In contrast with Models A, B and C presented above, these phase field models employ two order parameters, Ψ and Φ, which describe the difference in the local densities of the fluids and the local concentration of surfactants, respectively. An energy functional $F(\Psi, \Phi, \nabla\Psi, \nabla\Phi)$ of Ginzburg–Landau type is then prescribed and the order parameters satisfy evolution equations of Cahn–Hilliard type with respect to the energy functional F:

$$\partial_t \Psi = M_\Psi \Delta \mu_\Psi, \quad \partial_t \Phi = M_\Phi \Delta \mu_\Phi,$$

where $\mu_\Psi := \frac{\delta F}{\delta \Psi}$ and $\mu_\Phi := \frac{\delta F}{\delta \Phi}$ are the first variations of F with respect to Ψ and Φ, respectively and $M_\Psi, M_\Phi > 0$ represent the (constant) mobilities of Ψ and Φ, respectively.

Hydrodynamics can be introduced to the model by coupling the Cahn–Hilliard type equations for Ψ and Φ with the Navier–Stokes equations, leading to the model of van der Sman and van der Graaf [2006] (see also Appendix A of [Engbolm et al., 2013]):

$$\begin{aligned}
\nabla \cdot \boldsymbol{v} &= 0, \\
\rho(\partial_t \boldsymbol{v} + (\boldsymbol{v} \cdot \nabla)\boldsymbol{v}) &= -\nabla p + \nabla \cdot (2\eta D(\boldsymbol{v})) - \Phi \nabla \mu_\Phi - \Psi \nabla \mu_\Psi, \\
\partial_t \Psi + \boldsymbol{v} \cdot \nabla \Psi &= \nabla \cdot (M_\Psi \nabla \mu_\Psi), \\
\partial_t \Phi + \boldsymbol{v} \cdot \nabla \Phi &= \nabla \cdot (M_\Phi \nabla \mu_\Phi).
\end{aligned}$$

The form of μ_Φ and μ_Ψ will depend on the form of $F(\Psi, \nabla\Psi, \Phi, \nabla\Phi)$. For a detailed numerical comparison of phase field models of this type, we refer the reader to [Li and Kim, 2012].

We observe that parameters such as the surface tension σ and the kinetic factor measuring local thermodynamic equilibrium $\alpha^{(i)}$ do not appear explicitly in the twin order parameter type phase field models. In the derivation of the model equations, a desirable adsorption isotherm is first selected and the energy functional $F(\Psi, \Phi, \nabla\Psi, \nabla\Phi)$ is then constructed. The governing equations for Φ and Ψ are then derived and the surface tension will be given as a specific function of the surfactant concentration based on the chosen adsorption isotherm. We note that the chemical potential μ_Φ for the surfactants is a function of the phase order parameter Ψ, and

so one can identify the chemical potential for the surfactants in the two bulk phases and on the interface. Local thermodynamic equilibrium is achieved by equating the chemical potentials $\mu_\Phi(\Psi = +1) = \mu_\Phi(\Psi = -1) = \mu_\Phi(\Psi = 0)$ and rearranging gives the adsorption isotherm (see [Liu and Zhang, 2010]).

Among the aforementioned models with hydrodynamics, the model of van der Sman and van der Graaf [2006] can only achieve the Langmuir isotherm, while the model of Liu and Zhang [2010] can achieve both the Langmuir and the Frumkin isotherms. With regards to this, we remark that our phase field models are more flexible that these twin order parameters type phase field models at recovering isotherms in thermodynamic equilibrium, since our surfactant equations do not have to be re-derived in order to facilitate changing isotherm relations.

1.4 Sharp interface limits of the phase field models

In the phase field models, the width of the interfacial layer is characterised by the length scale over which the order parameter varies from its values at the bulk regions. A natural question is whether the phase field model can be related to the sharp interface model in the asymptotic limit in which this width is small compared to the length scales associated to the bulk regions. If so, one can also view the phase field methodology purely as a tool for approximating the sharp interface equations. If the objective is to ensure that, in the limit of vanishing interfacial thickness, certain sharp interface models are recovered then there is a lot of freedom in constructing phase field models to meet one's needs (see e.g. [Li et al., 2009]).

The results on the asymptotic limits of phase field models are broadly divided into two categories. One is based on formally matched asymptotic calculations, while the other consists of mathematically rigorous convergence results.

1.4.1 Formal asymptotics analysis

The procedure of formal asymptotic analysis is based on the assumption that there exist a family of solutions, sufficiently smooth and indexed by ε, to the diffuse interface models. For small ε, we assume that the domain Ω can at each time t be divided into two open subdomains $\Omega^{\pm}(t;\varepsilon)$, separated by an interface $\Gamma(t;\varepsilon)$. Furthermore, we assume that the solutions have asymptotic expansions in ε in the bulk regions (away from $\Gamma(t;\varepsilon)$) and another expansion in the interfacial regions (close to $\Gamma(t;\varepsilon)$). We denote the former as the outer expansions and the latter as the inner expansions. The idea is to analyse these expansions where they should match up in a suitable transition region. This method is formal in the sense that

it is not analysed further and it is not known whether the asymptotic expansions really exist and converge. Details of the method can be found in Caginalp [1989]; Fife and Penrose [1995]; Garcke and Stinner [2006]; Abels, Garcke, and Grün [2011] for the phase field models with the smooth double-well potential and in Blowey and Elliott [1993]; Cahn, Elliott, and Novick-Cohen [1996]; Bhate, Bower, and Kumar [2002] for phase field models with the double-obstacle potential.

The third contribution of this thesis is a formal asymptotic analysis of Models A, B and C with both the double-well and double-obstacle potentials. In Chapter 4, we highlight the differences in the analysis and show that Model A converges formally to the sharp interface model (1.2.1) - (1.2.7), while Models B and C converge formally to the case of one-sided and two-sided instantaneous adsorption, respectively. For Model A, by choosing $\alpha^{(i)}$ to scale with ε, we formally recover the sharp interface model with two-sided instantaneous adsorption. The analysis of this case is slightly non standard and the details are presented in Section 4.1.4.

We remark that it is unknown if the twin order parameter type phase field models such as the model of van der Sman and van der Graaf [2006] can be related to any sharp interface model in the limit of vanishing interfacial thickness.

1.4.2 Rigorous convergence results

The techniques for showing rigorous convergence of phase field models are divided into two main categories. The first method is to rigorously justify the formal asymptotic analysis, while the second is to show that weak solutions to the phase field models converge weakly to generalised solutions to the sharp interface equations.

Rigorous asymptotic analysis

The method of rigorous asymptotic analysis is based on constructing an approximating solution that almost satisfy the phase field equations (i.e. with an additional error term) and converges strongly to classical solutions to the sharp interface equations. This implies that classical solutions to the sharp interface model are required to apply this technique.

The construction of the approximating solution is derived from matching asymptotic expansions. Similar to the formal asymptotic analysis discussed above, an outer and an inner expansion in ε are used. By collecting terms of the same order of ε, we obtain systems of partial differential equations from the outer and inner expansions at each order of ε. To obtain solvability of the system, appropriate boundary conditions are prescribed by the matching conditions (in the sense that

there exists a region where both expansions are valid and hence should match up). This allows us to construct an expansion of arbitrary order in ε and it can be shown that this expansion satisfy the phase field equations with an additional "error" term.

Via some spectral estimates from Chen [1994], one can show that, as the order of the expansion increases, the error term can be made arbitrary small and hence the constructed expansion is arbitrary close to the solution to the phase field equations. Moreover, the leading order term in the expansion is constructed from the classical solution to the sharp interface equations. Hence, as $\varepsilon \to 0$, the solutions to the phase field equations converge strongly to the classical solution to the sharp interface equations.

We remark that this method has been successfully applied to the Allen–Cahn equation [De Mottoni and Schatzman, 1995], the Cahn–Hilliard equation [Alikakos et al., 1994; Carlen et al., 2005], and for a general phase field model [Caginalp and Chen, 1998].

Energy methods and weak convergence

One may also take advantage of the natural a priori estimates (or energy estimates) that some of the phase field models possess. These estimates provide uniform bounds on certain quantities and allow us to deduce compactness results. For instance, one observes that the Allen–Cahn equation

$$\varepsilon \partial_t \varphi_{AC} = \varepsilon \Delta \varphi_{AC} - \frac{1}{\varepsilon} W'(\varphi_{AC}), \text{ in } \Omega, \quad \nabla \varphi_{AC} \cdot \boldsymbol{\nu}_{\partial\Omega} = 0, \text{ on } \partial\Omega,$$

and the Cahn–Hilliard equation

$$\begin{aligned} \varepsilon \partial_t \varphi_{CH} = \Delta \mu, \quad \mu = -\varepsilon \Delta \varphi_{CH} + \frac{1}{\varepsilon} W'(\varphi_{CH}), \text{ in } \Omega, \\ \nabla \varphi_{CH} \cdot \boldsymbol{\nu}_{\partial\Omega} = \nabla \mu \cdot \boldsymbol{\nu}_{\partial\Omega} = 0, \text{ on } \partial\Omega, \end{aligned}$$

possess the following natural a priori estimate:

$$\begin{aligned} \int_\Omega \mathcal{E}_{GL}(\varphi_{AC}, \nabla \varphi_{AC})(t) + \int_0^t \int_\Omega \varepsilon \left| \partial_t \varphi_{AC} \right|^2 = \int_\Omega \mathcal{E}_{GL}(\varphi_{AC}, \nabla \varphi_{AC})(0), \\ \int_\Omega \mathcal{E}_{GL}(\varphi_{CH}, \nabla \varphi_{CH})(t) + \int_0^t \int_\Omega \left| \nabla \mu \right|^2 = \int_\Omega \mathcal{E}_{GL}(\varphi_{CH}, \nabla \varphi_{CH})(0). \end{aligned}$$

By prescribing appropriate initial data, so that the right hand side of the a priori estimates are bounded uniformly in ε, one can appeal to standard weak compactness results to deduce that the solutions to the phase field model converge

weakly in appropriate function spaces. The weak limit is then shown to be the weak/generalised solution of the sharp interface model.

In the radial symmetric case, rigorous convergence based on energy methods have been shown in Stoth [1996] for the Cahn–Hilliard equation and in Bronsard and Kohn [1991] for the Allen–Cahn equation. In Blowey and Elliott [1994], weak solutions to a phase field model with a double–obstacle potential are shown to converge to the weak solution to the classical Stefan problem.

In general, weak solutions to classical free boundary problems may develop singularities in finite time and it becomes unclear how to define classical solutions to the sharp interface problems. Brakke [1978] made a first attempt to define generalised solutions to motion by mean curvature, where the existence of a weak solution to the mean curvature flow is shown in the class of codimension-one varifolds. Subsequently, using energy bounds and techniques from geometric measure theory, Ilmanen [1993] showed that the weak solutions to the Allen–Cahn equation converges to mean curvature flow in the sense of Brakke [1978]. This technique has been successfully applied to the Cahn–Hilliard equation and its variants in Chen [1996]; Röger and Tonegawa [2008]; Garcke and Kwak [2006], and to a general phase field model in Soner [1995]. For two-phase flow, the convergence of weak solutions of the Abels, Garcke, and Grün [2011] model to varifold solutions of a Navier–Stokes/Mullin–Sekerka system has been shown in Abels and Lengeler [2013].

The energy method has also been applied in the setting of numerical approximation of phase field models. In a series of papers [Feng and Probl, 2003, 2004, 2005], Feng and Prohl have proposed various finite element approximations to phase field models that utilise spectral estimates of the Allen–Cahn and Cahn–Hilliard operators derived in Chen [1994] to establish useful a priori bounds that grow only in low polynomial order of ε^{-1}, under reasonable constraints on the underlying finite element mesh. They show that the fully discrete solutions converge to the solutions of the phase field models as the spatial and temporal mesh sizes tend to zero and, as a non-trivial byproduct, the fully discrete solution converges to classical solutions of the sharp interface models as ε converges to zero.

We remark that the fully discrete finite element approximations of the Navier–Stokes–Allen–Cahn model and the Navier–Stokes–Cahn–Hilliard model have been analysed in Feng, He, and Liu [2007] and Feng [2006], respectively. Existence of weak solutions to both models are shown via convergence of numerical solutions satisfying a discrete energy law. Furthermore, the numerical solutions can be shown to converge to regular solutions to the sharp interface problem, provided they exist.

As a first step to the rigorous convergence analysis of Models A, B and C,

the fourth contribution of this thesis is the analysis and convergence of a diffuse interface approximation to an elliptic coupled bulk-surface PDE system with the energy method. We will show, in Chapter 5, that the weak solutions $(u^\varepsilon, v^\varepsilon)$ to

$$\begin{aligned} -\nabla\cdot(\xi_\varepsilon \mathcal{A}^E \nabla u^\varepsilon) + \xi_\varepsilon a^E u^\varepsilon &= \xi_\varepsilon f^E + \delta_\varepsilon K(v^\varepsilon - u^\varepsilon), \text{ in } \Omega, \\ -\nabla\cdot(\delta_\varepsilon \mathcal{B}^E \nabla v^\varepsilon) + \delta_\varepsilon b^E v^\varepsilon &= \delta_\varepsilon \beta g^E - \delta_\varepsilon K(v^\varepsilon - u^\varepsilon), \text{ in } \Omega. \end{aligned} \tag{1.4.1}$$

converge to the weak solution (u, v) to

$$\begin{aligned} -\nabla\cdot(\mathcal{A}\nabla u) + au &= f, \text{ in } \Omega^{(1)}, \\ -\nabla_\Gamma\cdot(\mathcal{B}\nabla_\Gamma v) + bv + \mathcal{A}\nabla u\cdot\nu &= \beta g, \text{ on } \Gamma = \partial\Omega^{(1)}, \\ \mathcal{A}\nabla u\cdot\nu &= K(v-u), \text{ on } \Gamma. \end{aligned} \tag{1.4.2}$$

as $\varepsilon \to 0$, where $\Omega^{(1)}$ is a domain contained in Ω such that $\Gamma \cap \partial\Omega = \emptyset$, $\mathcal{A}^E$, a^E, f^E, $\mathcal{B}^E$, b^E, g^E are extensions of $\mathcal{A}$, a, f, $\mathcal{B}$, b, g to Ω, and ξ_ε and δ_ε are similar to the corresponding functions in Models A, B and C.

Sub- and super-solutions

For completeness, we mention the method of sub- and super-solutions, which will not be used in this thesis. For phase field models consisting of second order differential equations, the comparison principle provides another technique to show rigorous convergence to solutions of the sharp interface equations. The idea is to construct sub- and super-solutions to the phase field model using the classical solutions of the sharp interface equations. The comparison principle implies that the solution to the phase field model is bounded above and below by the super- and sub-solution, respectively, provided their initial conditions are related in a similar way. One can show that the Hausdorff distance between the zero-level set of the order parameter and the sharp interface hypersurface scales with ε.

This method has been applied predominantly to the Allen–Cahn equation and its variants, we refer to Evans et al. [1992]; Alfaro et al. [2008]; Chen [1992a,b]; Alfaro et al. [2010] for the Allen–Cahn equation with the double-well potential and Elliott and Schätzle [1997]; Chen and Elliott [1994]; Nochetto, Paolini, and Verdi [1993]; Nochetto and Verdi [1995] for the double-obstacle potential.

It is not known if this method is applicable to fourth order phase field models such as the Cahn–Hilliard equation and its variants as no comparison principle exists for fourth order problems.

1.5 Outline

The structure of this thesis is as follows:

In Chapter 2 we will derive the sharp interface model (1.2.1) – (1.2.7) from basic conservation laws. We show that the sharp interface model satisfies a local energy inequality and present the functional forms for γ and G that lead to six of the popular adsorption isotherms when $\alpha^{(i)} = 0$, namely those of Henry, Langmuir, Volmer, van der Waals, Frumkin, and Freundlich. We will outline several specific models that can be derived from the sharp interface model and present the non-dimensional equations.

In Chapter 3, we present the derivation of three phase field models based on the Lagrange multiplier method presented in Abels, Garcke, and Grün [2011] and show all of them satisfy a local dissipation inequality. We will also outline several specific models that can be derived from the phase field models and present the non-dimensional equations.

In Chapter 4 we show, via formally matched asymptotics, that we recover (1.2.1) – (1.2.7) from Model A and (1.2.8) from Models B and C in the limit $\varepsilon \to 0$. In addition, Model A can be shown to converge to the sharp interface problem with instantaneous adsorption when the kinetic term is chosen appropriately. We then present 1D and 2D numerical simulations to support the asymptotic analysis.

In Chapter 5 we analyse the convergence of (1.4.1) to (1.4.2) as a first step to rigorously justify the sharp interface limit of our diffuse interface models. Equation (1.4.1) is also known as the diffuse domain approximation of (1.4.2) (see Li et al. [2009]; Teigen et al. [2009, 2011]), and its derivation is similar to how we derive the phase field surfactant equations in Section 3.2. The well-posedness for (1.4.1) is shown using weighted Sobolev spaces, and under appropriate assumptions on ξ_ε and δ_ε, we prove that the solution to (1.4.1) converges to the solution to (1.4.2) as ε tends to zero. Our analysis also covers a general second order elliptic PDE with Dirichlet, Neumann or Robin boundary condition. We then present 1D and 2D numerical simulations to support the analysis.

In Appendix A, we will outline several facts regarding transport identities that will be useful in the derivation of the sharp interface model in Chapter 2. In Appendix B, we will use a result of Alt [2009] to derive the surfactant equations for the phase field models in Chapter 3. In Appendix C, we will list several important functional analytical results for the analysis in Chapter 5.

Chapter 2

Sharp Interface Models

We consider a domain $\Omega \subset \mathbb{R}^d$, $d = 1, 2, 3$, containing two immiscible, incompressible Newtonian fluids with possibly different constant mass densities $\overline{\rho}^{(i)}$, $i = 1, 2$. The domain occupied by the fluid with density $\overline{\rho}^{(i)}$ is labelled as $\Omega^{(i)} \subset \mathbb{R} \times \mathbb{R}^d$, where we set $\Omega^{(i)}(t) := \{x \in \Omega; (t, x) \in \Omega^{(i)}\}$. The two domains are separated by an interface Γ which is a hypersurface in $\mathbb{R} \times \mathbb{R}^d$ such that $\Gamma(t) \cap \partial\Omega = \emptyset$, where $\Gamma(t) := \{x \in \Omega; (t, x) \in \Gamma\}$. A surfactant is present which alters the surface tension by adsorbing to the fluid interface and, provided it is soluble in the corresponding fluid, it is subject to diffusion in the phases $\Omega^{(i)}$. We denote the fluid velocity field by $\boldsymbol{v}$, the pressure by p, the bulk surfactant densities by $c^{(i)}, i = 1, 2$, the interface surfactant density by c^Γ, and the corresponding bulk and interfacial free energy densities are denoted by $G_i(c^{(i)}), i = 1, 2$, and $\gamma(c^\Gamma)$, respectively.

2.1 Balance equations

Let $V(t)$ be an arbitrary material test volume in Ω with external unit normal $\boldsymbol{\nu}_{ext}$ of $V(t) \cap \Omega$. If $V(t) \cap \Gamma(t)$ is non-empty then we denote its external unit co-normal by $\boldsymbol{\mu}$ and write $\boldsymbol{\nu}_{ext}^{(i)}$ for the external unit normal of $V(t) \cap \Omega^{(i)}(t)$, $i = 1, 2$.

We make the following assumptions:

S1 The system is closed and is isothermal. There is no mass flux across the external boundary $\partial\Omega$ and no external bodily forces acting on the system.

S2 The fluids do not undergo phase transitions and satisfy the no-slip condition at the phase boundary $\Gamma(t)$.

S3 The fluid interface $\Gamma(t)$ does not intersect with the external boundary.

S4 In the fluid regions away from the interface, surfactants will be subjected to transport mechanisms consisting of only diffusion and convection.

S5 Close to the interface, surfactants will be subjected to adsorption mechanisms, as well as diffusion and convection.

S6 The mass of the surfactants relative to the mass of the fluid is negligible.

S7 The free energy densities G_i, γ are strictly convex, and the surface tension σ, defined as the Legendre transform of γ, is positive.

Let us briefly remark on the above assumptions. Assumptions S1, S2, S4 and S5 give us a reasonable starting point to begin modelling the dynamics of surfactants in fluid flow. In particular, one can relax Assumption S1 by allowing for external bodily forces or external fluid/surfactant mass fluxes, which would modify the sharp interface model by additional forcing terms or boundary conditions. In assuming S3, we neglect the effects of moving contact lines on the external boundary for simplicity. Assumption S6 is a physical assumption and Assumption S7 is a technical assumption, but also driven by physical reasoning. In particular, the surface tension is always positive, as zero surface tension between two phases would be an unrealistic situation.

By Assumption S1 and the Reynolds transport theorem (Theorem A.1), the balance of fluid mass inside the phases requires

$$0 = \frac{d}{dt}\int_{V(t)\cap\Omega^{(i)}} \overline{\rho}^{(i)} = \int_{V(t)\cap\Omega^{(i)}} \partial_t^\bullet \overline{\rho}^{(i)} + \overline{\rho}^{(i)} \nabla \cdot \boldsymbol{v},$$

where $\partial_t^\bullet$ denotes the material derivative (see Appendix A for a precise definition). Since $\overline{\rho}^{(i)}$ is constant, the arbitrariness of $V(t)$ leads to the pointwise conservation law

$$\nabla \cdot \boldsymbol{v} = 0. \tag{2.1.1}$$

By Assumption S6, the surfactants have a negligible effect on the momentum of the fluids, and so the conservation of linear and angular momentum becomes

$$\frac{d}{dt}\int_{V(t)\cap\Omega^{(i)}} \overline{\rho}^{(i)} \boldsymbol{v} = \int_{\partial(V(t)\cap\Omega^{(i)})} \boldsymbol{T}^{(i)} \boldsymbol{\nu}_{ext}^{(i)},$$

where $\boldsymbol{T}^{(i)}$, $i = 1, 2$, is the symmetric stress tensor. Application of Theorem A.1 and the divergence theorem, together with the arbitrariness of the test volume $V(t)$

lead to the pointwise conservation law:

$$\partial_t(\overline{\rho}^{(i)}\boldsymbol{v}) + \nabla\cdot(\overline{\rho}^{(i)}\boldsymbol{v}\otimes\boldsymbol{v}) = \partial_t^\bullet(\overline{\rho}^{(i)}\boldsymbol{v}) = \nabla\cdot\boldsymbol{T}^{(i)}. \tag{2.1.2}$$

These equations hold in $\Omega^{(1)}(t)\cup\Omega^{(2)}(t)$.

As the fluids do not undergo phase transitions, consequently there are no convective fluxes across the interface. Hence, the normal components of the fluid velocities are continuous across the interface $\Gamma(t)$ and match up with the normal velocity of interface (i.e., the interface is advected with the flow). Thus, by Assumption S2, we obtain

$$[\boldsymbol{v}]_1^2 = 0, \quad \boldsymbol{v}\cdot\boldsymbol{\nu} = u_\Gamma.$$

Here $[\cdot]_1^2$ denotes the jump of the quantity in brackets across Γ from $\Omega^{(1)}$ to $\Omega^{(2)}$, $\boldsymbol{\nu}$ is the unit outward normal of $\Gamma(t)$ pointing into $\Omega^{(2)}(t)$, and u_Γ is the normal velocity of the interface.

By Assumption S4, mass balance for bulk surfactants in a material test volume $V(t)$ away from the interface $\Gamma(t)$ yields

$$\frac{d}{dt}\int_{V(t)\cap\Omega^{(i)}} c^{(i)} = -\int_{\partial(V(t)\cap\Omega^{(i)})} \boldsymbol{J}_c^{(i)}\cdot\boldsymbol{\nu}_{ext},$$

where $\boldsymbol{J}_c^{(i)}$ is the bulk molecular flux. By Theorem A.1 and using that $\nabla\cdot\boldsymbol{v}=0$, this leads to the pointwise law

$$\partial_t^\bullet c^{(i)} + \nabla\cdot\boldsymbol{J}_c^{(i)} = 0, \quad i=1,2. \tag{2.1.3}$$

In light of Assumption S5, we postulate the balance of total surfactant mass in a test volume $V(t)$ intersecting $\Gamma(t)$ to be

$$\begin{aligned}&\frac{d}{dt}\left(\sum_{i=1,2}\int_{V(t)\cap\Omega^{(i)}(t)} c^{(i)} + \int_{V(t)\cap\Gamma(t)} c^\Gamma\right) \\ &= \sum_{i=1,2}\int_{\partial(V(t)\cap\Omega^{(i)}(t))\setminus\Gamma(t)} -\boldsymbol{J}_c^{(i)}\cdot\boldsymbol{\nu}_{ext} + \int_{\partial(V(t)\cap\Gamma(t))} -\boldsymbol{J}_\Gamma\cdot\boldsymbol{\mu},\end{aligned} \tag{2.1.4}$$

where $\boldsymbol{J}_\Gamma$ is the interfacial molecular flux, tangential to Γ. Using Theorem A.1, the surface transport theorem (Theorem A.6) and the surface divergence theorem

(Theorem A.8) we obtain

$$\begin{aligned}&\frac{d}{dt}\left(\sum_{i=1,2}\int_{V(t)\cap\Omega^{(i)}(t)} c^{(i)} + \int_{V(t)\cap\Gamma(t)} c^{\Gamma}\right)\\ =&\sum_{i=1}^{2}\int_{V(t)\cap\Omega^{(i)}(t)} \partial_t^{\bullet} c^{(i)} + \int_{V(t)\cap\Gamma(t)} \left(\partial_t^{\bullet} c^{\Gamma} + c^{\Gamma}\nabla_{\Gamma}\cdot\boldsymbol{v}\right)\end{aligned}$$

for the left hand side and

$$\begin{aligned}&\sum_{i=1,2} -\int_{\partial(V(t)\cap\Omega^{(i)}(t))\setminus\Gamma(t)} \boldsymbol{J}_c^{(i)}\cdot\boldsymbol{\nu}_{ext} - \int_{\partial(V(t)\cap\Gamma(t))} \boldsymbol{J}_{\Gamma}\cdot\boldsymbol{\mu}\\ =&\sum_{i=1,2} -\int_{\partial(V(t)\cap\Omega^{(i)}(t))} \boldsymbol{J}_c^{(i)}\cdot\boldsymbol{\nu}_{ext}^{(i)} - \int_{V(t)\cap\Gamma(t)} ([\boldsymbol{J}_c^{(i)}]_1^2\boldsymbol{\nu} + \nabla_{\Gamma}\cdot\boldsymbol{J}_{\Gamma})\end{aligned}$$

for the right hand side. Hence, using (2.1.3) and the mass balance (2.1.4) yield the following pointwise law for the interfacial surfactant:

$$\partial_t^{\bullet} c^{\Gamma} + c^{\Gamma}\nabla_{\Gamma}\cdot\boldsymbol{v} = -\nabla_{\Gamma}\cdot\boldsymbol{J}_{\Gamma} - [\boldsymbol{J}_c^{(i)}]_1^2\boldsymbol{\nu}, \tag{2.1.5}$$

where $[\boldsymbol{J}_c^{(i)}]_1^2\boldsymbol{\nu}$ is the mass flux for the transfer of surfactant to the interface from the adjacent sub-layers. When the mass flux is zero and the interfacial molecular flux is modelled by Fick's law, $\boldsymbol{J}_{\Gamma} = -D_s\nabla_{\Gamma}c^{\Gamma}$, we obtain the classical mass balance equation for interfacial surfactants derived in Scriven [1960]; Aris [1962]; Stone [1990]; Wong et al. [1996].

2.2 Energy inequality

We postulate a total energy of the form

$$\mathcal{E}_{SI} := \sum_{i=1,2}\int_{\Omega^{(i)}(t)} [\tfrac{\overline{\rho}^{(i)}}{2}|\boldsymbol{v}|^2 + G_i(c^{(i)})] + \int_{\Gamma(t)} \gamma(c^{\Gamma}), \tag{2.2.1}$$

By Assumption S7, the Legendre transform of the surface energy density γ is well defined, and the density dependent surface tension $\sigma(c^{\Gamma})$ is defined as

$$\sigma(c^{\Gamma}) := \gamma(c^{\Gamma}) - c^{\Gamma}\gamma'(c^{\Gamma}). \tag{2.2.2}$$

Let $V(t)$ be an arbitrary material test volume. Then, by Theorem A.1 and Theorem A.6,

$$\frac{d}{dt}\left(\sum_{i=1}^{2}\int_{V(t)\cap\Omega^{(i)}(t)}(\tfrac{\overline{\rho}^{(i)}}{2}\,|\boldsymbol{v}|^2+G_i(c^{(i)}))+\int_{V(t)\cap\Gamma(t)}\gamma(c^\Gamma)\right)$$
$$=\sum_{i=1}^{2}\int_{V(t)\cap\Omega^{(i)}(t)}\left(\overline{\rho}^{(i)}\boldsymbol{v}\cdot\partial_t^\bullet\boldsymbol{v}+G_i'(c^{(i)})\partial_t^\bullet c^{(i)}\right)+\int_{V(t)\cap\Gamma(t)}\left(\gamma'(c^\Gamma)\partial_t^\bullet c^\Gamma+\gamma(c^\Gamma)\nabla_\Gamma\cdot\boldsymbol{v}\right).$$

Using (2.1.2), (2.1.3), (2.1.5), (2.2.2), and the following identity for a vector field $\boldsymbol{v}$ and a second order tensor $\boldsymbol{T}$ (with $\boldsymbol{T}^\perp$ denoting the transpose of $\boldsymbol{T}$):

$$(\nabla\cdot\boldsymbol{T})\cdot\boldsymbol{v}=\nabla\cdot(\boldsymbol{T}^\perp\boldsymbol{v})-\nabla\boldsymbol{v}\colon\boldsymbol{T},$$

we obtain

$$\begin{aligned}\frac{d}{dt}\mathcal{E}_{SI}=&\sum_{i=1}^{2}\int_{V(t)\cap\Omega^{(i)}(t)}\left(\nabla\cdot((\boldsymbol{T}^{(i)})^\perp\boldsymbol{v}-G_i'(c^{(i)})\boldsymbol{J}_c^{(i)})-\boldsymbol{T}^{(i)}\colon\nabla\boldsymbol{v}+\nabla G_i'(c^{(i)})\cdot\boldsymbol{J}_c^{(i)}\right)\\&+\int_{V(t)\cap\Gamma(t)}\gamma'(c^\Gamma)(-\nabla_\Gamma\cdot\boldsymbol{J}_\Gamma-[\boldsymbol{J}_c^{(i)}]_1^2\boldsymbol{\nu})+\sigma(c^\Gamma)\nabla_\Gamma\cdot\boldsymbol{v}.\end{aligned}$$

Application of the divergence theorem then leads to

$$\begin{aligned}\frac{d}{dt}\mathcal{E}_{SI}=&\sum_{i=1}^{2}\int_{V(t)\cap\Omega^{(i)}(t)}-\boldsymbol{T}^{(i)}\colon\nabla\boldsymbol{v}+\nabla G_i'(c^{(i)})\cdot\boldsymbol{J}_c^{(i)}+\int_{\partial(V(t)\cap\Gamma(t))}-\gamma'(c^\Gamma)\boldsymbol{J}_\Gamma\cdot\boldsymbol{\mu}\\&+\sum_{i=1}^{2}\int_{\partial(V(t)\cap\Omega^{(i)}(t))\setminus\Gamma(t)}((\boldsymbol{T}^{(i)})^\perp\boldsymbol{v}-G_i'(c^{(i)})\boldsymbol{J}_c^{(i)})\cdot\boldsymbol{\nu}_{ext}\\&+\int_{V(t)\cap\Gamma(t)}((\boldsymbol{T}^{(1)})^\perp\boldsymbol{v}-G_1'(c^{(1)})\boldsymbol{J}_c^{(1)})\cdot\boldsymbol{\nu}+((\boldsymbol{T}^{(2)})^\perp\boldsymbol{v}-G_2'(c^{(2)})\boldsymbol{J}_c^{(2)})\cdot(-\boldsymbol{\nu})\\&+\int_{V(t)\cap\Gamma(t)}\boldsymbol{J}_\Gamma\cdot\nabla_\Gamma\gamma'(c^\Gamma)+\gamma'(c^\Gamma)(\boldsymbol{J}_c^{(1)}\cdot\boldsymbol{\nu}-\boldsymbol{J}_c^{(2)}\cdot\boldsymbol{\nu})+\sigma(c^\Gamma)\nabla_\Gamma\cdot\boldsymbol{v}.\end{aligned}$$

Decomposing the velocity field $\boldsymbol{v}$ on $\Gamma(t)$ into its normal and tangential components,

$$\boldsymbol{v}=u_\Gamma\boldsymbol{\nu}+\boldsymbol{v}_\tau,$$

then gives

$$\int_{V(t)\cap\Gamma(t)}\sigma(c^\Gamma)\nabla_\Gamma\cdot(u_\Gamma\boldsymbol{\nu}+\boldsymbol{v}_\tau)=\int_{V(t)\cap\Gamma(t)}\sigma(c^\Gamma)(\underbrace{\nabla_\Gamma u_\Gamma\cdot\boldsymbol{\nu}}_{=0}+\underbrace{u_\Gamma\nabla_\Gamma\cdot\boldsymbol{\nu}}_{-\kappa u_\Gamma}+\nabla_\Gamma\cdot\boldsymbol{v}_\tau)$$
$$=\int_{V(t)\cap\Gamma(t)}-\sigma(c^\Gamma)\kappa u_\Gamma-\nabla_\Gamma\sigma(c^\Gamma)\cdot\boldsymbol{v}+\int_{\partial(V(t)\cap\Gamma(t))}\sigma(c^\Gamma)\boldsymbol{v}_\tau\cdot\boldsymbol{\mu},$$

where $\kappa = -\nabla_\Gamma \cdot \boldsymbol{\nu}$ is the mean curvature and we have used integration by parts (Theorem A.7) to obtain the last equality (we have also implicitly used $\nabla_\Gamma \sigma(c^\Gamma) \cdot \boldsymbol{\nu} = 0$ to obtain $\nabla_\Gamma \sigma(c^\Gamma) \cdot \boldsymbol{v}_\tau = \nabla_\Gamma \sigma(c^\Gamma) \cdot \boldsymbol{v}$). Altogether we have

$$\begin{aligned}
\frac{d}{dt}\mathcal{E}_{SI} =& \sum_{i=1}^{2} \int_{\partial(V(t)\cap\Omega^{(i)}(t))\setminus\Gamma(t)} ((\boldsymbol{T}^{(i)})^\perp \boldsymbol{v} - G_i'(c^{(i)})\boldsymbol{J}_c^{(i)}) \cdot \boldsymbol{\nu}_{ext} \\
&+ \int_{\partial(V(t)\cap\Gamma(t))} \left(-\gamma'(c^\Gamma)\boldsymbol{J}_\Gamma \cdot \boldsymbol{\mu} + \sigma(c^\Gamma)\boldsymbol{v}_\tau \cdot \boldsymbol{\mu}\right) \\
&+ \sum_{i=1}^{2} \int_{V(t)\cap\Omega^{(i)}(t)} \left(-\boldsymbol{T}^{(i)} : \nabla \boldsymbol{v} + \nabla G_i'(c^{(i)}) \cdot \boldsymbol{J}_c^{(i)}\right) + \int_{V(t)\cap\Gamma(t)} \boldsymbol{J}_\Gamma \cdot \nabla_\Gamma \gamma'(c^\Gamma) \\
&+ \int_{V(t)\cap\Gamma(t)} \left((\gamma'(c^\Gamma) - G_1'(c^{(1)}))\boldsymbol{J}_c^{(1)} \cdot \boldsymbol{\nu} - (\gamma'(c^\Gamma) - G_2'(c^{(2)}))\boldsymbol{J}_c^{(2)} \cdot \boldsymbol{\nu}\right) \\
&+ \int_{V(t)\cap\Gamma(t)} \left(\boldsymbol{T}^{(1)}\boldsymbol{\nu} \cdot \boldsymbol{v} - \boldsymbol{T}^{(2)}\boldsymbol{\nu} \cdot \boldsymbol{v} - \sigma(c^\Gamma)\kappa \boldsymbol{v} \cdot \boldsymbol{\nu} - \nabla_\Gamma \sigma(c^\Gamma) \cdot \boldsymbol{v}\right).
\end{aligned}$$

Hence, if we choose

$$\begin{aligned}
\boldsymbol{J}_c^{(i)} \cdot \nabla G_i'(c^{(i)}) &\le 0, && \text{in } \Omega^{(i)}(t), \quad i = 1, 2, \\
\boldsymbol{T}^{(i)} : \nabla \boldsymbol{v} &\ge 0, && \text{in } \Omega^{(i)}(t), \quad i = 1, 2, \\
\boldsymbol{J}_\Gamma \cdot \nabla_\Gamma \gamma'(c^\Gamma) &\le 0, && \text{on } \Gamma(t), \\
(\boldsymbol{J}_c^{(1)} \cdot \boldsymbol{\nu})(\gamma'(c^\Gamma) - G_1'(c^{(1)})) &\le 0, && \text{on } \Gamma(t), \\
(-\boldsymbol{J}_c^{(2)} \cdot \boldsymbol{\nu})(\gamma'(c^\Gamma) - G_2'(c^{(2)})) &\le 0, && \text{on } \Gamma(t), \\
(-[\boldsymbol{T}]_1^2\boldsymbol{\nu} - \sigma(c^\Gamma)\kappa\boldsymbol{\nu} - \nabla_\Gamma \sigma(c^\Gamma)) \cdot \boldsymbol{v} &\le 0, && \text{on } \Gamma(t),
\end{aligned}$$

then we obtain the following energy inequality:

$$\begin{aligned}
\frac{d}{dt}\mathcal{E}_{SI} \le& \sum_{i=1}^{2} \left(\int_{\partial(V(t)\cap\Omega^{(i)}(t))\setminus\Gamma(t)} ((\boldsymbol{T}^{(i)})^\perp \boldsymbol{v} - G_i'(c^{(i)})\boldsymbol{J}_c^{(i)}) \cdot \boldsymbol{\nu}_{ext} \right) \\
&+ \int_{\partial(V(t)\cap\Gamma(t))} \left(-\gamma'(c^\Gamma)\boldsymbol{J}_\Gamma \cdot \boldsymbol{\mu} + \sigma(c^\Gamma)\boldsymbol{v}_\tau \cdot \boldsymbol{\mu}\right),
\end{aligned}$$

where the right hand side represents the working on the arbitrary material test volume $V(t)$ and the inequality indicates that the dissipation is non-negative, thus guaranteeing thermodynamic consistency (see [Fried and Gurtin, 1993; Gurtin et al., 1996]).

2.3 General models

We make the following constitutive assumptions:

$$\begin{aligned}
\boldsymbol{J}_c^{(i)} &= -M_c^{(i)}(c^{(i)})\nabla G_i'(c^{(i)}),\\
\boldsymbol{J}_\Gamma &= -M_\Gamma(c^\Gamma)\nabla_\Gamma\gamma'(c^\Gamma),\\
\alpha^{(i)}(c^\Gamma,c^{(i)})(-1)^{i+1}\boldsymbol{J}_c^{(i)}\cdot\boldsymbol{\nu} &= -(\gamma'(c^\Gamma)-G_i'(c^{(i)})),\\
\boldsymbol{T}^{(i)} &= -p\boldsymbol{I}+2\eta^{(i)}D(\boldsymbol{v}),\\
-[\boldsymbol{T}]_1^2\boldsymbol{\nu} &= \sigma(c^\Gamma)\kappa\boldsymbol{\nu}+\nabla_\Gamma\sigma(c^\Gamma),
\end{aligned} \tag{2.3.1}$$

where $M_c^{(i)}(c^{(i)})>0$, $M_\Gamma(c^\Gamma)>0$, and $\alpha^{(i)}(c^\Gamma,c^{(i)})\geq 0$.

The formulation presented in (2.3.1) utilises a free energy approach, first applied to the kinetics of surfactant adsorption in Diamant and Andelman [1996]; Diamant, Ariel, and Andelman [2001], to model instantaneous adsorption kinetics. At adsorption/desorption equilibrium, the chemical potentials $\gamma'(c^\Gamma)$ and $G'(c)$ must be equal [Zhdanov, 2001; Liu and Zhang, 2010; van der Sman and van der Graaf, 2006] and thus this approach allows us to cover the adsorption isotherms often used in the literature by selecting suitable functional forms for γ and G. Hence, $\alpha^{(i)}>0$ can be seen as a kinetic factor which relates the speed of adsorption to the interface or desorption from the interface to the deviation from local thermodynamical equilibrium. Let us summarise the governing equations of the general model for two-phase flow with soluble surfactant: For $i=1,2$,

$$\nabla\cdot\boldsymbol{v}=0,\ \text{in}\ \Omega^{(i)}(t), \tag{2.3.2}$$

$$\partial_t(\overline{\rho}^{(i)}\boldsymbol{v})+\nabla\cdot(p\boldsymbol{I}-2\eta^{(i)}D(\boldsymbol{v})+\overline{\rho}^{(i)}\boldsymbol{v}\otimes\boldsymbol{v})=0,\ \text{in}\ \Omega^{(i)}(t), \tag{2.3.3}$$

$$\partial_t^\bullet c^{(i)}-\nabla\cdot(M_c^{(i)}\nabla G_i'(c^{(i)}))=0,\ \text{in}\ \Omega^{(i)}(t), \tag{2.3.4}$$

$$[\boldsymbol{v}]_1^2=0,\quad \boldsymbol{v}\cdot\boldsymbol{\nu}=u_\Gamma,\ \text{on}\ \Gamma(t), \tag{2.3.5}$$

$$[p]_1^2\boldsymbol{\nu}-2[\eta^{(i)}D(\boldsymbol{v})]_1^2\boldsymbol{\nu}=\sigma(c^\Gamma)\kappa\boldsymbol{\nu}+\nabla_\Gamma\sigma(c^\Gamma),\ \text{on}\ \Gamma(t), \tag{2.3.6}$$

$$\partial_t^\bullet c^\Gamma+c^\Gamma\nabla_\Gamma\cdot\boldsymbol{v}=\nabla_\Gamma\cdot(M_\Gamma\nabla_\Gamma\gamma'(c^\Gamma))+[M_c^{(i)}\nabla G_i'(c^{(i)})]_1^2\boldsymbol{\nu},\ \text{on}\ \Gamma(t), \tag{2.3.7}$$

$$\alpha^{(i)}(-1)^i M_c^{(i)}\nabla G_i'(c^{(i)})\cdot\boldsymbol{\nu}=-(\gamma'(c^\Gamma)-G_i'(c^{(i)})),\ \text{on}\ \Gamma(t). \tag{2.3.8}$$

2.4 Specific models

2.4.1 Fick's law for fluxes

By appropriate choice of the mobilities we obtain Fick's law for the surfactant both in the bulk and on the surface. If we set

$$M_c^{(i)}(c^{(i)}) = D_c^{(i)} \frac{1}{G_i''(c^{(i)})}, \quad M_\Gamma(c^\Gamma) = D_\Gamma \frac{1}{\gamma''(c^\Gamma)},$$

for constant Fickian diffusivities $D_c^{(i)}, D_\Gamma > 0$. Then

$$\boldsymbol{J}_c^{(i)} = -D_c^{(i)} \nabla c^{(i)}, \quad \boldsymbol{J}_\Gamma = -D_\Gamma \nabla_\Gamma c^\Gamma.$$

2.4.2 Instantaneous adsorption and local equilibrium

We may assume that the process of adsorption of surfactant at the interface is instantaneous, i.e. fast compared to the timescale of convective and diffusive transport. This local equilibrium corresponds to the case that the bulk chemical potential $G'(c)$ and the interface chemical potential $\gamma'(c^\Gamma)$ are equal, i.e. we set $\alpha = 0$ in (2.3.1) (we here only consider one of the bulk phases adjacent to the interface and, for simplicity, drop the upper index (i)). We obtain the following relation (also see [Bothe and Prüss, 2010; Bothe et al., 2005]):

$$\gamma'(c^\Gamma) = G'(c) \quad \Longleftrightarrow \quad c^\Gamma = g(c) := (\gamma')^{-1}(G'(c)), \tag{2.4.1}$$

where $g : \mathbb{R}_+ \to \mathbb{R}_+$ is strictly increasing. This function g plays the role of various adsorption isotherms which state the equilibrium relations between the two densities.

Table 2.1 displays the functional forms for γ and G in order to obtain the adsorption isotherms of Henry, Langmuir, Volmer, van der Waals, Freundlich, and Frumkin (also see Table 7.2, pg. 201 of [Kralchevsky et al., 2008]). The free energies are (variants of) ideal solutions. Here, c_M^Γ is the maximum surfactant density on the interface, K a constant relating the surface density to the bulk density in equilibrium, σ_0 denotes the surface tension of a clean interface, B essentially is the sensitivity of the surface tension to surfactant, A in the Frumkin isotherm and the van der Waals isotherm is known as the surface interaction parameter while, in the Freundlich isotherm, A_c measures the adsorbent capacity and N is the intensity of adsorption.

Isotherm	Henry	Langmuir
Relation	$Kc = \frac{c^\Gamma}{c_M^\Gamma}$	$Kc = \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma}$
$\gamma(c^\Gamma) - \sigma_0$	$Bc^\Gamma(\log \frac{c^\Gamma}{c_M^\Gamma} - 1)$	$B\left(c^\Gamma \log \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma} + c_M^\Gamma \log(1 - \frac{c^\Gamma}{c_M^\Gamma})\right)$
$G(c)$	$Bc(\log(Kc) - 1)$	$Bc(\log(Kc) - 1)$
$\sigma - \sigma_0$	$-Bc^\Gamma$	$Bc_M^\Gamma \log\left(1 - \frac{c^\Gamma}{c_M^\Gamma}\right)$
Isotherm	Volmer	van der Waals
Relation	$Kc = \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma} \exp\left(\frac{c^\Gamma}{c_M^\Gamma - c^\Gamma}\right)$	$Kc = \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma} \exp\left(\frac{c^\Gamma}{c_M^\Gamma - c^\Gamma} - \frac{Ac^\Gamma}{B}\right)$
$\gamma(c^\Gamma) - \sigma_0$	$Bc^\Gamma \log \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma}$	$Bc^\Gamma \log \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma} - \frac{A(c^\Gamma)^2}{2}$
$G(c)$	$Bc \log(Kc)$	$Bc(\log(Kc) - 1)$
$\sigma - \sigma_0$	$-B\frac{c^\Gamma c_M^\Gamma}{c_M^\Gamma - c^\Gamma}$	$\frac{A(c^\Gamma)^2}{2} - B\frac{c^\Gamma c_M^\Gamma}{c_M^\Gamma - c^\Gamma}$
Isotherm	Freundlich	Frumkin
Relation	$Kc = \frac{1}{A_c}\left(\frac{c^\Gamma}{c_M^\Gamma}\right)^N$	$Kc = \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma} \exp\left(-\frac{Ac^\Gamma}{B}\right)$
$\gamma(c^\Gamma) - \sigma_0$	$NBc^\Gamma(\log \frac{c^\Gamma}{c_M^\Gamma} - 1)$	$B\left(c^\Gamma \log \frac{c^\Gamma}{c_M^\Gamma - c^\Gamma} + c_M^\Gamma \log \frac{c_M^\Gamma - c^\Gamma}{c_M^\Gamma}\right) - \frac{A(c^\Gamma)^2}{2}$
$G(c)$	$Bc(\log(A_c^N Kc) - 1)$	$Bc(\log(Kc) - 1)$
$\sigma - \sigma_0$	$-NBc^\Gamma$	$\frac{A(c^\Gamma)^2}{2} + Bc_M^\Gamma \log\left(1 - \frac{c^\Gamma}{c_M^\Gamma}\right)$

Table 2.1: Possible functional forms for γ and G to obtain the most frequently used adsorption isotherms and equations of state.

2.4.3 Insoluble surfactants

Neglecting (2.3.4), (2.3.8), and the jump term in (2.3.7) gives a two-phase flow model with insoluble surfactant. This coincides with the model of insoluble surfactants studied in James and Lowengrub [2004]; Elliott et al. [2011]; Xu et al. [2006]; Lai et al. [2008]; Khatri and Tornberg [2011].

2.4.4 Reformulation of the surfactant equations

The strong form of the surfactant equations (2.3.4), (2.3.7), (2.3.8) can be reformulated into an equivalent distributional form using a result from Alt [2009]. Let $\chi_{\Omega^{(i)}}$ and δ_Γ denote the distributions given by the Dirac measures on $\Omega^{(i)}$ and Γ

respectively; see Appendix B for a precise definition. We now define

$$j_1 = \frac{1}{\alpha^{(1)}}(\gamma'(c^\Gamma) - G_1'(c^{(1)})), \quad j_2 = \frac{1}{\alpha^{(2)}}(\gamma'(c^\Gamma) - G_2'(c^{(2)})).$$

In Appendix B we show that

$$\partial_t(\chi_{\Omega^{(1)}}c^{(1)}) + \nabla\cdot(\chi_{\Omega^{(1)}}c^{(1)}\boldsymbol{v} - \chi_{\Omega^{(1)}}M_c^{(1)}\nabla G_1'(c^{(1)})) = \delta_\Gamma j_1, \tag{2.4.2}$$

$$\partial_t(\chi_{\Omega^{(2)}}c^{(2)}) + \nabla\cdot(\chi_{\Omega^{(2)}}c^{(1)}\boldsymbol{v} - \chi_{\Omega^{(2)}}M_c^{(2)}\nabla G_2'(c^{(2)})) = \delta_\Gamma j_2, \tag{2.4.3}$$

$$\partial_t(\delta_\Gamma c^\Gamma) + \nabla\cdot(\delta_\Gamma c^\Gamma\boldsymbol{v} - M_\Gamma\delta_\Gamma\nabla\gamma'(c^\Gamma)) = -\delta_\Gamma(j_1+j_2), \tag{2.4.4}$$

interpreted in their distributional formulations are equivalent to

$$\begin{aligned}
\partial_t c^{(1)} + \nabla\cdot(c^{(1)}\boldsymbol{v} - M_c^{(1)}\nabla G_1'(c^{(1)})) &= 0, \text{ in } \Omega^{(1)},\\
M_c^{(1)}\nabla G_1'(c^{(1)})\cdot\boldsymbol{\nu} &= j_1, \text{ on } \Gamma,\\
\partial_t c^{(2)} + \nabla\cdot(c^{(2)}\boldsymbol{v} - M_c^{(2)}\nabla G_2'(c^{(2)})) &= 0, \text{ in } \Omega^{(2)},\\
-M_c^{(2)}\nabla G_2'(c^{(2)})\cdot\boldsymbol{\nu} &= j_2, \text{ on } \Gamma,
\end{aligned}$$

and (2.3.7) respectively.

2.5 Non-dimensional evolution equations

To derive equations in a dimensionless form we pick a length scale L, a time scale T (or, equivalently, a scale for the velocity $V = L/T$), a scale Σ for the surface tension, and let $C^\Gamma = L^{-2}, C = L^{-3}$ denote scales for the surfactant densities in the interface and in the bulk, respectively.

The Reynolds number, as the ratio of advective to viscous forces, is defined as $\mathrm{Re} := (\overline{\rho}^{(2)}L^2)/(\eta^{(2)}T)$. The capillary number, as the ratio of viscous to surface tension forces, is defined as $\mathrm{Ca} = (\eta^{(2)}L)/(T\Sigma)$. Scaling the pressure by $T^2/(\overline{\rho}^{(2)}L^2)$ we arrive at the following dimensionless fluid equations:

$$\begin{aligned}
\nabla_*\cdot\boldsymbol{v}_* &= 0, \text{ in } \Omega^{(i)}(t),\\
\partial_{t_*}(\overline{\rho}^{\pm}\boldsymbol{v}_*) + \nabla_*\cdot\left(p_*\boldsymbol{I} - \frac{2\eta^\pm}{\mathrm{Re}}D(\boldsymbol{v}_*) + \overline{\rho}^\pm\boldsymbol{v}_*\otimes\boldsymbol{v}_*\right) &= 0, \text{ in } \Omega^{(i)}(t),\\
[\boldsymbol{v}_*]_1^2 = 0, \quad \boldsymbol{v}_*\cdot\boldsymbol{\nu} &= u_{\Gamma_*}, \text{ on } \Gamma(t),\\
\left[p_*\boldsymbol{I} - \frac{2\eta^\pm}{\mathrm{Re}}D(\boldsymbol{v}_*)\right]_1^2\boldsymbol{\nu} &= \frac{1}{\mathrm{ReCa}}(\sigma_*\kappa\boldsymbol{\nu} + \nabla_{\Gamma_*}\sigma_*), \text{ on } \Gamma(t),
\end{aligned}$$

where $\eta^+ = 1$, $\eta^- = \eta^{(1)}/\eta^{(2)}$, $\overline{\rho}^+ = 1$, $\overline{\rho}^- = \overline{\rho}^{(1)}/\overline{\rho}^{(2)}$. Let

$$\gamma_* = \frac{\gamma}{\Sigma}, \quad G_{i,*} = \frac{G_i L}{\Sigma}, \quad M_{c,*}^{(i)} = M_c^{(i)} \Sigma T L^3, \quad M_{\Gamma,*} = M_\Gamma \Sigma T L^2,$$

where $\gamma_*, G_{i,*}$ denote the dimensionless free energies and $M_{c,*}^{(i)}, M_{\Gamma,*}$ denote the dimensionless mobilities. The dimensionless surfactant equations are given by

$$\begin{aligned}
\partial_{t_*}^\bullet c_*^{(i)} - \nabla_* \cdot \left(M_{c,*}^{(i)} \nabla_* G_{i,*}'(c_*^{(i)}) \right) &= 0, \text{ in } \Omega^{(i)}(t), \\
\partial_{t_*}^\bullet c_*^\Gamma + c_*^\Gamma \nabla_{\Gamma_*} \cdot \boldsymbol{v}_* - \nabla_{\Gamma_*} \cdot \left(M_{\Gamma,*} \nabla_{\Gamma_*} \gamma_*'(c_*^\Gamma) \right) &= \left[M_{c,*}^{(i)} \nabla_* G_{i,*}'(c_*^{(i)}) \right]_1^2 \boldsymbol{\nu}, \text{ on } \Gamma(t), \\
\alpha_*^{(i)} (-1)^i M_{c,*}^{(i)} \nabla_* G_i'(c_*^{(i)}) \cdot \boldsymbol{\nu} &= -(\gamma_*'(c_*^\Gamma) - G_{*,i}'(c_*^{(i)})), \text{ on } \Gamma(t),
\end{aligned}$$

where $\alpha_*^{(i)} = \alpha^{(i)}/(T\Sigma L^4)$ is the dimensionless kinetic factor. If we consider the mobilities in Section 2.4.1, then we have the relation

$$M_{c,*}^{(i)} = \frac{1}{\mathrm{Pe}_{c,i}} \frac{1}{G_{i,*}''(c_*^{(i)})}, \quad M_{\Gamma,*} = \frac{1}{\mathrm{Pe}_\Gamma} \frac{1}{\gamma_*''(c_*^\Gamma)},$$

where $\mathrm{Pe}_{c,i} = L^2/(TD_c^{(i)})$, as the ratio of advection to diffusion of bulk surfactants, is the bulk Peclet number and $\mathrm{Pe}_\Gamma = L^2/(TD_\Gamma)$ is the corresponding interface Peclet number. The dimensionless surfactant equations with Fickian diffusion read as

$$\begin{aligned}
\partial_{t_*}^\bullet c_*^{(i)} - \nabla_* \cdot \left(\frac{1}{\mathrm{Pe}_{c,i}} \nabla_* c_*^{(i)} \right) &= 0, \text{ in } \Omega^{(i)}(t), \\
\partial_{t_*}^\bullet c_*^\Gamma + c_*^\Gamma \nabla_{\Gamma_*} \cdot \boldsymbol{v}_* - \nabla_{\Gamma_*} \cdot \left(\frac{1}{\mathrm{Pe}_\Gamma} \nabla_{\Gamma_*} c_*^\Gamma \right) &= \left[\frac{1}{\mathrm{Pe}_{c,i}} \nabla_* c_*^{(i)} \right]_1^2 \boldsymbol{\nu}, \text{ on } \Gamma(t), \\
\alpha_*^{(i)} \frac{(-1)^i}{\mathrm{Pe}_{c,i}} \nabla_* c_*^{(i)} \cdot \boldsymbol{\nu} &= -(\gamma_*'(c_*^\Gamma) - G_{*,i}'(c_*^{(i)})), \text{ on } \Gamma(t).
\end{aligned}$$

Chapter 3

Phase Field Models

3.1 Model for two-phase fluid flow

In this chapter we will derive a phase field model for two-phase flow with surfactant generalizing the work by Abels, Garcke, and Grün [2011] on phase field modelling of two-phase flow.

For a test volume $V \subset \Omega$, let ρ denote the total mass density of the mixture in V and, for $i = 1, 2$, denote by $\overline{\rho}^{(i)}, \eta^{(i)}, V_i$ the constant bulk density, constant viscosity and the volume occupied by fluid i in V, respectively. Let $u_i = V_i/V$ denote the volume fraction occupied by fluid i in V and the local densities of fluid i in V is then given by $u_i\overline{\rho}^{(i)}$.

Mirroring the assumptions in Chapter 2, we make the following assumptions for the phase field setup:

P1 The system is closed and is isothermal. There is no mass flux across the external boundary $\partial\Omega$ and no external bodily forces acting on the system.

P2 There is no excess volume due to mixing.

P3 The inertia and kinetic energy due to the motion of the constituent fluids relative to the gross motion of the mixture fluid is negligible.

P4 The mass flux in the bulk regions consists only of advection, and we allow mass diffusion into the other fluid in the interfacial region. The sum of these two contributions gives the total mass flux of the constituent fluid.

P5 The mass of the surfactants relative to the mass of the fluid is negligible.

P6 The free energy densities G_i, γ of $c^{(i)}, c^{\Gamma}$ are strictly convex, and the surface tension σ, defined as the Legendre transform of γ, is positive.

P7 There exists a dissipation inequality for the total energy density e with energy flux $\boldsymbol{J}_e$ such that for all test volume $V(t)$ with external normal $\boldsymbol{\nu}_{ext}$ that is transported with the flow,

$$\frac{d}{dt}\int_{V(t)} e + \int_{\partial V(t)} \boldsymbol{J}_e \cdot \boldsymbol{\nu}_{ext} \leq 0.$$

By Assumption P2, we have

$$u_1 + u_2 = 1. \tag{3.1.1}$$

Then the total density ρ can be expressed as a function of the difference in volume fraction $\varphi = u_2 - u_1$, which is a natural choice for the order parameter that distinguishes the two fluids,

$$\rho = \rho(\varphi) = \frac{\overline{\rho}^{(2)}(1+\varphi)}{2} + \frac{\overline{\rho}^{(1)}(1-\varphi)}{2} = \frac{\overline{\rho}^{(2)} - \overline{\rho}^{(1)}}{2}\varphi + \frac{\overline{\rho}^{(2)} + \overline{\rho}^{(1)}}{2}. \tag{3.1.2}$$

Similarly, we define

$$\eta(\varphi) = \frac{\eta^{(2)} - \eta^{(1)}}{2}\varphi + \frac{\eta^{(2)} + \eta^{(1)}}{2} \tag{3.1.3}$$

to be the interpolation between two bulk viscosities $\eta^{(1)}$ and $\eta^{(2)}$.

Let $\boldsymbol{v}$ denote the fluid velocity, which we will specify later and let $\hat{\boldsymbol{J}}_i$, $i = 1, 2$, denote the total mass flux of fluid i. Then, by Assumption P4, the mass flux in the bulk regions for fluid i is given by $\overline{\rho}^{(i)} u_i \boldsymbol{v}$. We introduce the diffusive flux $\overline{\boldsymbol{J}}_i$, $i = 1, 2$, for diffusion into the other fluid in the interfacial region. Then the mass flux in the interfacial region is given by $\overline{\rho}^{(i)}\overline{\boldsymbol{J}}_i$, so that

$$\hat{\boldsymbol{J}}_i = \overline{\rho}^{(i)}(u_i \boldsymbol{v} + \overline{\boldsymbol{J}}_i). \tag{3.1.4}$$

For $i = 1, 2$, conservation of mass of fluid i then yields the following local law

$$\partial_t(\overline{\rho}^{(i)} u_i) + \nabla \cdot \left(\overline{\rho}^{(i)} u_i \boldsymbol{v}\right) + \nabla \cdot \left(\overline{\rho}^{(i)} \overline{\boldsymbol{J}}_i\right) = 0, \tag{3.1.5}$$

which upon cancelling the constant $\overline{\rho}^{(i)}$ gives

$$\partial_t u_i + \nabla \cdot (u_i \boldsymbol{v}) + \nabla \cdot \overline{\boldsymbol{J}}_i = 0. \tag{3.1.6}$$

Subtracting leads to the equation for the order parameter φ:

$$\partial_t \varphi + \nabla \cdot (\varphi \boldsymbol{v}) + \nabla \cdot (\overline{\boldsymbol{J}}_2 - \overline{\boldsymbol{J}}_1) = 0, \tag{3.1.7}$$

while adding (3.1.6) for $i = 1, 2$ and using (3.1.1), we have

$$\nabla \cdot \boldsymbol{v} = -\nabla \cdot \left(\overline{\boldsymbol{J}}_1 + \overline{\boldsymbol{J}}_2 \right). \tag{3.1.8}$$

Furthermore, using the relation $\rho = u_1 \overline{\rho}^{(1)} + u_2 \overline{\rho}^{(2)}$, we obtain from (3.1.5)

$$\partial_t \rho + \nabla \cdot (\rho \boldsymbol{v}) + \nabla \cdot (\overline{\rho}^{(1)} \overline{\boldsymbol{J}}_1 + \overline{\rho}^{(2)} \overline{\boldsymbol{J}}_2) = 0. \tag{3.1.9}$$

We define the individual velocity field for fluid i by $\boldsymbol{v}_i = \hat{\boldsymbol{J}}_i / (\overline{\rho}^{(i)} u_i)$ and choose $\boldsymbol{v}$ to be the volume averaged velocity of the mixture:

$$\boldsymbol{v} = u_1 \boldsymbol{v}_1 + u_2 \boldsymbol{v}_2 = \frac{\hat{\boldsymbol{J}}_1}{\overline{\rho}^{(1)}} + \frac{\hat{\boldsymbol{J}}_2}{\overline{\rho}^{(2)}}.$$

Then using (3.1.4) we obtain from the definition of $\boldsymbol{v}_i$,

$$u_i \boldsymbol{v}_i = u_i \boldsymbol{v} + \overline{\boldsymbol{J}}_i,$$

and upon summing for $i = 1, 2$ and using (3.1.1) we obtain

$$u_1 \boldsymbol{v}_1 + u_2 \boldsymbol{v}_2 = \boldsymbol{v} + \overline{\boldsymbol{J}}_1 + \overline{\boldsymbol{J}}_2 \Longrightarrow 0 = \overline{\boldsymbol{J}}_1 + \overline{\boldsymbol{J}}_2, \tag{3.1.10}$$

i.e., we obtain conservation of volume due to interfacial diffusion. Furthermore, by (3.1.8),

$$\nabla \cdot \boldsymbol{v} = 0, \tag{3.1.11}$$

and we obtain the incompressibility condition with respect to the volume averaged velocity.

We remark that this differs from the approach in Antanovskii [1995]; Lowengrub and Truskinovsky [1998], where a mass-averaged velocity $\tilde{\boldsymbol{v}}$, given by $\rho \tilde{\boldsymbol{v}} = \overline{\rho}^{(1)} u_1 \boldsymbol{v}_1 + \overline{\rho}^{(2)} u_2 \boldsymbol{v}_2 = \hat{\boldsymbol{J}}_1 + \hat{\boldsymbol{J}}_2$ is chosen. By (3.1.4), this implies that

$$\rho \tilde{\boldsymbol{v}} = (\overline{\rho}^{(1)} u_1 + \overline{\rho}^{(2)} u_2) \tilde{\boldsymbol{v}} + \overline{\rho}^{(1)} \overline{\boldsymbol{J}}_1 + \overline{\rho}^{(2)} \overline{\boldsymbol{J}}_2 = \rho \tilde{\boldsymbol{v}} + \overline{\rho}^{(1)} \overline{\boldsymbol{J}}_1 + \overline{\rho}^{(2)} \overline{\boldsymbol{J}}_2.$$

Hence, the choice of a mass-averaged velocity leads to $\overline{\rho}^{(1)} \overline{\boldsymbol{J}}_1 + \overline{\rho}^{(2)} \overline{\boldsymbol{J}}_2 = 0$, i.e. the

sum of the mass diffusive flow is zero, and consequently,

$$\partial_t \rho + \nabla \cdot (\rho \tilde{\boldsymbol{v}}) = -\nabla \cdot (\overline{\rho}^{(1)} \overline{\boldsymbol{J}}_1 + \overline{\rho}^{(2)} \overline{\boldsymbol{J}}_2) = 0.$$

So, the classical equation for ρ is recovered, but by (3.1.8),

$$\nabla \cdot \tilde{\boldsymbol{v}} = -\nabla \cdot (\overline{\boldsymbol{J}}_1 + \overline{\boldsymbol{J}}_2) = \Big(\frac{\overline{\rho}^{(2)}}{\overline{\rho}^{(1)}} - 1\Big) \nabla \cdot \overline{\boldsymbol{J}}_2.$$

The mass averaged velocity $\tilde{\boldsymbol{v}}$ can be non divergence-free if there is diffusion in the interfacial regions. We refer to Ding, Spelt, and Shu [2007] for a discussion involving the two choices of velocity.

As in Abels, Garcke, and Grün [2011]; Gurtin, Polignone, and Viñals [1996], Assumption P3 allows us to consider the mixture as a single fluid with the volume averaged velocity $\boldsymbol{v}$. By Assumption P5, conservation of linear momentum with respect to the velocity field $\boldsymbol{v}$ reads

$$\partial_t(\rho \boldsymbol{v}) + \nabla \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v}) = (\partial_t^\bullet \rho)\boldsymbol{v} + \rho(\partial_t^\bullet \boldsymbol{v}) = \nabla \cdot \boldsymbol{T}, \tag{3.1.12}$$

where $\boldsymbol{T}$ is a tensor yet to be specified.

From (3.1.10), we set

$$\boldsymbol{J}_\varphi := \overline{\boldsymbol{J}}_2 - \overline{\boldsymbol{J}}_1 = 2\overline{\boldsymbol{J}}_2, \quad \overline{\boldsymbol{J}} := \overline{\rho}^{(2)} \overline{\boldsymbol{J}}_2 + \overline{\rho}^{(1)} \overline{\boldsymbol{J}}_1 = (\overline{\rho}^{(2)} - \overline{\rho}^{(1)}) \overline{\boldsymbol{J}}_2.$$

Then, from (3.1.7), (3.1.9), (3.1.11), and (3.1.12), the prototype diffuse interface model for incompressible two-phase flow with different densities is

$$\nabla \cdot \boldsymbol{v} = 0, \tag{3.1.13}$$

$$\partial_t(\rho \boldsymbol{v}) + \nabla \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v}) = \nabla \cdot \boldsymbol{T}, \tag{3.1.14}$$

$$\partial_t \varphi + \nabla \cdot (\varphi \boldsymbol{v}) = -\nabla \cdot \boldsymbol{J}_\varphi, \tag{3.1.15}$$

$$\partial_t \rho + \nabla \cdot (\rho \boldsymbol{v}) = -\nabla \cdot \overline{\boldsymbol{J}}, \tag{3.1.16}$$

where $\boldsymbol{J}_\varphi$ is a flux related to the mass flux $\overline{\boldsymbol{J}}$ by

$$(\overline{\rho}^{(2)} - \overline{\rho}^{(1)}) \boldsymbol{J}_\varphi = 2\overline{\boldsymbol{J}}. \tag{3.1.17}$$

Our goal is now to extend this model to the case where surfactants are present, distinguishing the cases of instantaneous and non-instantaneous adsorption. We proceed as in the sharp interface setting by postulating appropriate mass balance

equation(s) for the surfactant and deriving models from constitutive assumptions such that thermodynamic consistency is guaranteed.

3.2 Non-instantaneous adsorption (Model A)

3.2.1 Mass balance equations

We will use the distributional forms for the bulk and interfacial surfactant equations in the sharp interface model to derive the phase field surfactant equations. Since the sharp interface is replaced by an interfacial layer, we consider regularisations of $\chi_{\Omega^{(i)}}$ and δ_Γ that appear in (2.4.2), (2.4.3), (2.4.4). In the context of phase field models, many regularisations of δ_Γ are available from the literature [Teigen et al., 2011; Elliott et al., 2011; Rätz and Voigt, 2006; Lee and Junseok, 2012], but it will turn out that the Ginzburg–Landau free energy density

$$\frac{\varepsilon}{2}\left|\nabla\varphi\right|^2 + \frac{1}{\varepsilon}W(\varphi)$$

is a suitable regularisation for a multiple of δ_Γ. We define

$$\delta(\varphi, \nabla\varphi) := \mathcal{W}\left(\frac{\varepsilon}{2}\left|\nabla\varphi\right|^2 + \frac{1}{\varepsilon}W(\varphi)\right), \tag{3.2.1}$$

where $\mathcal{W}$ is a calibration constant that depends on the choice of the potential W, chosen such that $\delta(\varphi, \nabla\varphi)$ regularises δ_Γ (see [Modica and Mortola, 1977]). In particular, for the two choices of W discussed in Section 1.3.1, we set

$$\frac{1}{\mathcal{W}} = \begin{cases} \displaystyle\int_{-\infty}^{\infty} 2W(\tanh(\tfrac{z}{\sqrt{2}}))dz = \frac{2\sqrt{2}}{3}, & \text{for double-well potential,} \\ \displaystyle\int_{\frac{-\pi}{2}}^{\frac{\pi}{2}} 2W(\sin(z))dz = \frac{\pi}{2}, & \text{for double-obstacle potential.} \end{cases} \tag{3.2.2}$$

For the regularisation of $\chi_{\Omega^{(2)}}$, we consider $\xi_2(\varphi)$ to be a non-negative cut-off function such that $\xi_2(1) = 1$, $\xi_2(-1) = 0$, and ξ_2 varies smoothly across $|\varphi| < 1$. For example, in the subsequent numerical experiments we used

$$\xi_2(\varphi) = \frac{1}{2}(1+\varphi) \quad \text{or} \quad \begin{cases} 1, & \text{if } \varphi \geq 1, \\ \frac{1}{2}(1 + \frac{1}{2}\varphi(3-\varphi^2)), & \text{if } |\varphi| < 1, \\ 0, & \text{if } \varphi \leq -1. \end{cases}$$

Similarly, $\xi_1(\varphi) = 1 - \xi_2(\varphi)$ will be the regularisation of $\chi_{\Omega^{(1)}}$.

Our ansatz for the case of non-instantaneous adsorption of the surfactant to the interface is motivated by the distributional formulation in (2.4.2)-(2.4.4) and the diffuse domain approach [Li et al., 2009; Rätz and Voigt, 2006]. We replace the distributions δ_Γ and $\chi_{\Omega^{(i)}}$ with the regularisations $\delta(\varphi, \nabla\varphi)$ and $\xi_i(\varphi)$ and obtain

$$\partial_t(\xi_i(\varphi)c^{(i)}) + \nabla\cdot(\xi_i(\varphi)c^{(i)}\boldsymbol{v}) + \nabla\cdot(\xi_i(\varphi)\boldsymbol{J}_c^{(i)}) = \delta(\varphi,\nabla\varphi)j_i, \quad i=1,2, \tag{3.2.3}$$

$$\partial_t(\delta(\varphi,\nabla\varphi)c^\Gamma) + \nabla\cdot(\delta(\varphi,\nabla\varphi)c^\Gamma\boldsymbol{v}) + \nabla\cdot\Big(\delta(\varphi,\nabla\varphi)\boldsymbol{J}_\Gamma\Big) = -\delta(\varphi,\nabla\varphi)(j_1+j_2), \tag{3.2.4}$$

where $\boldsymbol{J}_c^{(i)}$ is the bulk surfactant flux, $\boldsymbol{J}_\Gamma$ is the interfacial surfactant flux and j_i, $i=1,2$, denote the mass exchange between the bulk and the interfacial regions.

In the above prototype model we allow the situation where there are surfactants present either in both bulk phases or in just one bulk phase. We denote the former as the two-sided model and the latter as the one-sided model. In the one-sided model, we set $c^{(1)} \equiv 0$, $\xi_1(\varphi) \equiv 0$, $j_1 \equiv 0$, $\boldsymbol{J}_{c,1} \equiv \boldsymbol{0}$ and we drop the subscripts so that equations (3.2.3), (3.2.4) are written as

$$\begin{aligned}\partial_t(\xi(\varphi)c) + \nabla\cdot(\xi(\varphi)c\boldsymbol{v}) + \nabla\cdot(\xi(\varphi)\boldsymbol{J}_c) &= \delta(\varphi,\nabla\varphi)j,\\ \partial_t\Big(\delta(\varphi,\nabla\varphi)c^\Gamma\Big) + \nabla\cdot(\delta(\varphi,\nabla\varphi)c^\Gamma\boldsymbol{v}) + \nabla\cdot\Big(\delta(\varphi,\nabla\varphi)\boldsymbol{J}_\Gamma\Big) &= -\delta(\varphi,\nabla\varphi)j.\end{aligned}$$

Observe that, for a test volume $V(t)$ with external normal $\boldsymbol{\nu}$ that is transported with the flow, by (3.2.3), (3.2.4), Theorem A.1 and the divergence theorem, we have

$$\frac{d}{dt}\Big(\sum_{i=1,2}\int_{V(t)}\xi_i c^{(i)} + \int_{V(t)}\delta c^\Gamma\Big) = -\int_{\partial V(t)}(\xi_1\boldsymbol{J}_c^{(1)} + \xi_2\boldsymbol{J}_c^{(2)} + \delta\boldsymbol{J}_\Gamma)\cdot\boldsymbol{\nu},$$

which is analogous to (2.1.4).

3.2.2 Energy inequality

As in the sharp interface setting and in analogy to (2.2.1) the total energy in a test volume V is the sum of the kinetic and free energy:

$$\int_V e(\boldsymbol{v},\varphi,\nabla\varphi,c^{(i)},c^\Gamma) = \int_V \rho\frac{|\boldsymbol{v}|^2}{2} + \delta(\varphi,\nabla\varphi)\gamma(c^\Gamma) + \sum_{i=1,2}\xi_i(\varphi)G_i(c^{(i)}). \tag{3.2.5}$$

Since $\delta(\varphi,\nabla\varphi)$ approximates δ_Γ we can consider $\delta(\varphi,\nabla\varphi)\gamma(c^\Gamma)$ as an approximation of the surface free energy density. By Assumption P7 and Theorem A.1, the following

dissipation law holds pointwise in V:

$$-\mathcal{D} := \partial_t e + \nabla \cdot (\boldsymbol{v} e) + \nabla \cdot \boldsymbol{J}_e \leq 0, \tag{3.2.6}$$

where $\boldsymbol{J}_e$ is an energy flux that we will determine later.

Using (3.1.13), (3.1.14), (3.1.16), and the identities

$$\begin{aligned}
\nabla \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v}) \cdot \boldsymbol{v} &= (\nabla \rho \cdot \boldsymbol{v}) \, |\boldsymbol{v}|^2 + \rho \nabla \cdot \Big(\tfrac{|\boldsymbol{v}|^2}{2} \boldsymbol{v} \Big), \\
[\nabla \cdot (\boldsymbol{v} \otimes \overline{\boldsymbol{J}})] \cdot \boldsymbol{v} &= (\nabla \boldsymbol{v} \cdot \overline{\boldsymbol{J}}) \cdot \boldsymbol{v} + |\boldsymbol{v}|^2 \, \nabla \cdot \overline{\boldsymbol{J}}, \\
\nabla \cdot (\boldsymbol{T}^\perp \boldsymbol{v}) &= (\nabla \cdot \boldsymbol{T}) \cdot \boldsymbol{v} + \boldsymbol{T} \colon \nabla \boldsymbol{v},
\end{aligned}$$

we have

$$\begin{aligned}
\partial_t \Big(\tfrac{\rho |\boldsymbol{v}|^2}{2} \Big) + \nabla \cdot \Big(\tfrac{\rho |\boldsymbol{v}|^2}{2} \boldsymbol{v} \Big) &= -\tfrac{|\boldsymbol{v}|^2}{2} \nabla \cdot \overline{\boldsymbol{J}} + \rho (\partial_t \boldsymbol{v}) \cdot \boldsymbol{v} + \rho \nabla \cdot \Big(\tfrac{|\boldsymbol{v}|^2}{2} \boldsymbol{v} \Big) \\
&= -\tfrac{|\boldsymbol{v}|^2}{2} \nabla \cdot \overline{\boldsymbol{J}} + [\partial_t (\rho \boldsymbol{v}) + \nabla \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v})] \cdot \boldsymbol{v} - [\partial_t \rho + \nabla \rho \cdot \boldsymbol{v}] \, |\boldsymbol{v}|^2 \\
&= -\tfrac{|\boldsymbol{v}|^2}{2} \nabla \cdot \overline{\boldsymbol{J}} + (\nabla \cdot \boldsymbol{T}) \cdot \boldsymbol{v} + [(\nabla \cdot \overline{\boldsymbol{J}}) \boldsymbol{v}] \cdot \boldsymbol{v} \\
&= -\tfrac{|\boldsymbol{v}|^2}{2} \nabla \cdot \overline{\boldsymbol{J}} + (\nabla \cdot \boldsymbol{T}) \cdot \boldsymbol{v} + [\nabla \cdot (\boldsymbol{v} \otimes \overline{\boldsymbol{J}})] \cdot \boldsymbol{v} - [(\overline{\boldsymbol{J}} \cdot \nabla \boldsymbol{v})] \cdot \boldsymbol{v} \\
&= \nabla \cdot \Big(-\tfrac{|\boldsymbol{v}|^2}{2} \overline{\boldsymbol{J}} + \boldsymbol{T}^\perp \boldsymbol{v} \Big) - \boldsymbol{T} \colon \nabla \boldsymbol{v} + [\nabla \cdot (\boldsymbol{v} \otimes \overline{\boldsymbol{J}})] \cdot \boldsymbol{v} \\
&= \nabla \cdot \Big(-\tfrac{|\boldsymbol{v}|^2}{2} \overline{\boldsymbol{J}} + (\boldsymbol{T}^\perp + [\boldsymbol{v} \otimes \overline{\boldsymbol{J}}]^\perp) \boldsymbol{v} \Big) - (\boldsymbol{T} + (\boldsymbol{v} \otimes \overline{\boldsymbol{J}})) \colon \nabla \boldsymbol{v}.
\end{aligned}$$

We use the identities

$$\begin{aligned}
\partial_t^\bullet \nabla \varphi &= \nabla \partial_t^\bullet \varphi - (\nabla \boldsymbol{v})^\perp \nabla \varphi, \quad \partial_t^\bullet (ab) = a \partial_t^\bullet b + b \partial_t^\bullet a, \\
\partial_t^\bullet (\delta(\varphi, \nabla \varphi) \gamma(c^\Gamma)) &= \partial_t^\bullet (\delta) \gamma(c^\Gamma) + \gamma'(c^\Gamma) \partial_t^\bullet (c^\Gamma) \delta \\
&= \partial_t^\bullet (\delta) \gamma(c^\Gamma) + \gamma'(c^\Gamma) \partial_t^\bullet (\delta c^\Gamma) - \gamma'(c^\Gamma) c^\Gamma \partial_t^\bullet (\delta), \\
\partial_t^\bullet (\xi_i(\varphi) G_i(c^{(i)})) &= \partial_t^\bullet (\xi_i c^{(i)}) G_i'(c^{(i)}) + \partial_t^\bullet (\xi_i) (G_i(c^{(i)}) - c^{(i)} G_i'(c^{(i)}))
\end{aligned}$$

to obtain after some lengthy calculations that

$$\begin{aligned}
-\mathcal{D} = {} & \nabla \cdot \Big(\boldsymbol{J}_e - \overline{\boldsymbol{J}} \tfrac{|\boldsymbol{v}|^2}{2} + \boldsymbol{T}^\perp \boldsymbol{v} + (\boldsymbol{v} \otimes \overline{\boldsymbol{J}}) \boldsymbol{v} \Big) \\
& + \nabla \cdot \Big(-\delta \gamma'(c^\Gamma) \boldsymbol{J}_\Gamma - \sum_{i=1,2} \xi_i G_i'(c^{(i)}) \boldsymbol{J}_c^{(i)} + \mathcal{W} \varepsilon \sigma \nabla \varphi \partial_t^\bullet \varphi \Big) \\
& + \nabla \cdot \Big(\boldsymbol{J}_\varphi \Big(\sum_{i=1,2} \xi_i'(\varphi) (G_i(c^{(i)}) - G_i'(c^{(i)}) c^{(i)}) - \nabla \cdot (\mathcal{W} \varepsilon \sigma \nabla \varphi) + \frac{\mathcal{W}}{\varepsilon} \sigma W'(\varphi) \Big) \Big) \\
& + \delta \boldsymbol{J}_\Gamma \cdot \nabla \gamma'(c^\Gamma) + \xi_1 \boldsymbol{J}_c^{(1)} \cdot \nabla G_1'(c^{(1)}) + \xi_2 \boldsymbol{J}_c^{(2)} \cdot \nabla G_2'(c^{(2)})
\end{aligned}$$

$$
\begin{aligned}
&- \delta j_1(\gamma'(c^\Gamma) - G_1'(c^{(1)})) - \delta j_2(\gamma'(c^\Gamma) - G_2'(c^{(2)}))\\
&+ \boldsymbol{J}_\varphi \cdot \nabla\Big(\sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)}) - \nabla\cdot(\mathcal{W}\varepsilon\sigma\nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\sigma W'(\varphi)\Big)\\
&- \nabla\boldsymbol{v}\colon \Big(\varphi\Big(\sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)}) - \nabla\cdot(\mathcal{W}\varepsilon\sigma\nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\sigma W'(\varphi)\Big)\Big)\boldsymbol{I}\\
&+ \nabla\boldsymbol{v}\colon \Big(\delta\sigma + \xi_1(G_1(c^{(1)}) - G_1'(c^{(1)})c^{(1)}) + \xi_2(G_2(c^{(2)}) - G_2'(c^{(2)})c^{(2)})\Big)\boldsymbol{I}\\
&- \nabla\boldsymbol{v}\colon (\boldsymbol{T} + \boldsymbol{v}\otimes\overline{\boldsymbol{J}} + \mathcal{W}\varepsilon\sigma\nabla\varphi\otimes\nabla\varphi).
\end{aligned}
$$

In the case where the surfactant is present in only one of the bulk phases, a similar calculation shows that we obtain the above form for $-\mathcal{D}$ without any terms involving the subscript 1.

3.2.3 Constitutive assumptions

We choose $\boldsymbol{J}_e$ so that the divergence term in the calculation of $-\mathcal{D}$ cancels. For convenience, we set

$$
\mu = -\nabla\cdot\big(\mathcal{W}\varepsilon\sigma(c^\Gamma)\nabla\varphi\big) + \frac{\mathcal{W}}{\varepsilon}\sigma(c^\Gamma)W'(\varphi) + \sum_{i=1,2}\xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)}) \tag{3.2.7}
$$

and make the following constitutive assumptions:

$$
\boldsymbol{J}_\Gamma = -M_\Gamma(c^\Gamma)\nabla\gamma'(c^\Gamma), \tag{3.2.8}
$$

$$
\boldsymbol{J}_c^{(i)} = -M_c^{(i)}(c^{(i)})\nabla G_i'(c^{(i)}), \tag{3.2.9}
$$

$$
j_i = \frac{1}{\alpha^{(i)}}\big(\gamma'(c^\Gamma) - G_i'(c^{(i)})\big), \tag{3.2.10}
$$

$$
\boldsymbol{J}_\varphi = -m(\varphi)\nabla\mu, \tag{3.2.11}
$$

for some non-negative function $m(\varphi)$. Moreover, motivated by the calculation of $-\mathcal{D}$, we choose the tensor $\boldsymbol{T}$ to be

$$
\begin{aligned}
\boldsymbol{T} = &\Big(\sigma\delta + \sum_{i=1,2}\xi_i(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)}) - \varphi\mu\Big)\boldsymbol{I}\\
&- \boldsymbol{v}\otimes\overline{\boldsymbol{J}} - \mathcal{W}\varepsilon\sigma\nabla\varphi\otimes\nabla\varphi + 2\eta(\varphi)D(\boldsymbol{v}) - p\boldsymbol{I},
\end{aligned}
$$

where p denotes the unknown pressure, $\eta(\varphi) > 0$ denotes the viscosity defined in (3.1.3). From (3.1.17) the volume diffuse flux $\overline{\boldsymbol{J}}$ is given by

$$\overline{\boldsymbol{J}} = -\tfrac{\overline{\rho}^{(2)}-\overline{\rho}^{(1)}}{2} m(\varphi)\nabla\mu.$$

Since the interface thickness will be of order ε, it turns out that the term

$$\nabla\cdot(\sigma(\delta(\varphi,\nabla\varphi)\boldsymbol{I} - \mathcal{W}\varepsilon\nabla\varphi\otimes\nabla\varphi))$$

scales with ε^{-2}, while the term

$$\nabla\cdot(\xi_1(G_1(c^{(1)}) - G_1'(c^{(1)})c^{(1)})\boldsymbol{I} + \xi_2(G_2(c^{(2)}) - G_2'(c^{(2)})c^{(2)})\boldsymbol{I} - \varphi\mu\boldsymbol{I})$$

scales with ε^{-1}, the same order as the pressure p. Hence we absorb the latter term as part of the pressure and reuse the variable p as the rescaled pressure, leading to

$$\boldsymbol{T} = \sigma(c^\Gamma)(\delta(\varphi,\nabla\varphi)\boldsymbol{I} - \mathcal{W}\varepsilon\nabla\varphi\otimes\nabla\varphi) - p\boldsymbol{I} + 2\eta(\varphi)D(\boldsymbol{v}) - \boldsymbol{v}\otimes\overline{\boldsymbol{J}}. \tag{3.2.12}$$

We remark that the term $\nabla\cdot(\sigma\delta(\varphi,\nabla\varphi)\boldsymbol{I})$ in the momentum equation is required to recover the surface gradient of the surface tension in the asymptotic analysis. It is present also in other diffuse interface models with Marangoni effects [Sun et al., 2009; Kim, 2005; Liu et al., 2005].

With the above assumptions we obtain the energy inequality

$$\begin{aligned}-\mathcal{D} =& -m(\varphi)\left|\nabla\mu\right|^2 - \sum_{i=1,2} M_c^{(i)}(c^{(i)})\xi_i(\varphi)\left|\nabla G_i'(c^{(i)})\right|^2 - 2\eta(\varphi)\left|D(\boldsymbol{v})\right|^2\\ &- \sum_{i=1,2}\frac{1}{\alpha^{(i)}}\delta(\varphi,\nabla\varphi)\left|\gamma'(c^\Gamma) - G_i'(c^{(i)})\right|^2 - M_\Gamma(c^\Gamma)\delta(\varphi,\nabla\varphi)\left|\nabla\gamma'(c^\Gamma)\right|^2 \le 0,\end{aligned}$$

and from (3.1.13), (3.1.14), (3.1.15), (3.2.3), and (3.2.4) with (3.2.7), (3.2.8), (3.2.9), (3.2.10), (3.2.11), and (3.2.12), the diffuse interface model (denoted Model A) for the case of non-instantaneous adsorption reads

$$\nabla\cdot\boldsymbol{v} = 0, \tag{3.2.13}$$

$$\begin{aligned}\partial_t(\rho\boldsymbol{v}) + \nabla\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{v}) =& \nabla\cdot\Big(-p\boldsymbol{I} + 2\eta(\varphi)D(\boldsymbol{v}) + \boldsymbol{v}\otimes\tfrac{\overline{\rho}^{(2)}-\overline{\rho}^{(1)}}{2}m(\varphi)\nabla\mu\Big)\\ &+ \nabla\cdot\big(\sigma(c^\Gamma)(\delta(\varphi,\nabla\varphi)\boldsymbol{I} - \mathcal{W}\varepsilon\nabla\varphi\otimes\nabla\varphi)\big),\end{aligned} \tag{3.2.14}$$

$$\partial_t^\bullet\varphi = \nabla\cdot(m(\varphi)\nabla\mu), \tag{3.2.15}$$

$$\mu = -\nabla\cdot(\mathcal{W}\varepsilon\sigma(c^\Gamma)\nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\sigma(c^\Gamma)W'(\varphi) \tag{3.2.16}$$

$$+ \sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)}),$$

$$\partial_t^\bullet(\xi_i(\varphi)c^{(i)}) = \nabla \cdot (M_c^{(i)}(c^{(i)})\xi_i(\varphi)\nabla G_i'(c^{(i)})) \tag{3.2.17}$$
$$+ \frac{1}{\alpha^{(i)}}\delta(\varphi, \nabla\varphi)(\gamma'(c^\Gamma) - G_i'(c^{(i)})), \quad i = 1, 2,$$

$$\partial_t^\bullet(\delta(\varphi, \nabla\varphi)c^\Gamma) = \nabla \cdot \Big(M_\Gamma(c^\Gamma)\delta(\varphi, \nabla\varphi)\nabla\gamma'(c^\Gamma)\Big) \tag{3.2.18}$$
$$- \delta(\varphi, \nabla\varphi) \sum_{i=1,2} \frac{1}{\alpha^{(i)}}(\gamma'(c^\Gamma) - G_i'(c^{(i)})).$$

3.3 Instantaneous adsorption, one-sided (Model B)

To model one-sided instantaneous adsorption, we assume that the bulk surfactant in $\Omega^{(2)}$ and the interface surfactant are in local thermodynamical equilibrium and we impose the constraint

$$\gamma'(c^\Gamma) = G_2'(c^{(2)}) \tag{3.3.1}$$

in order to replace c^Γ.

For this purpose, since γ' is strictly monotone (recall that γ is strictly convex by Assumption P6) we may set

$$c^\Gamma = (\gamma')^{-1}(G_2'(c^{(2)})) =: g(c^{(2)}).$$

We then consider one surfactant mass balance equation which we obtain by adding (3.2.3) for $i = 2$ and (3.2.4):

$$\begin{aligned}
&\partial_t^\bullet(\xi_1(\varphi)c^{(1)}) + \nabla \cdot (\xi_1(\varphi)\boldsymbol{J}_c^{(1)}) = \delta(\varphi, \nabla\varphi)j_1,\\
&\partial_t^\bullet(\xi_2(\varphi)c^{(2)} + \delta(\varphi, \nabla\varphi)g(c^{(2)})) + \nabla \cdot (\xi_2(\varphi)\boldsymbol{J}_c^{(2)} + \delta(\varphi, \nabla\varphi)\boldsymbol{J}_\Gamma) = -\delta(\varphi, \nabla\varphi)j_1,
\end{aligned} \tag{3.3.2}$$

in place of (3.2.3) and (3.2.4).

The energy density of the system is given by

$$e(\boldsymbol{v}, \varphi, \nabla\varphi, c^{(i)}) = \frac{1}{2}\rho\,|\boldsymbol{v}|^2 + \delta(\varphi, \nabla\varphi)\gamma(g(c^{(2)})) + \xi_1(\varphi)G_1(c^{(1)}) + \xi_2(\varphi)G_2(c^{(2)}),$$

and we set

$$\mu = -\nabla \cdot (\mathcal{W}\varepsilon\sigma(g)\nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\sigma(g)W'(\varphi) + \sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)}), \tag{3.3.3}$$

where

$$\sigma(g) = \gamma(g(c^{(2)})) - \gamma'(g(c^{(2)}))g(c^{(2)}) = \gamma(g(c^{(2)})) - G_2'(c^{(2)})g(c^{(2)}).$$

Then, a similar computation as in the previous model yields

$$\begin{aligned}
-\mathcal{D} &= \nabla \cdot \Big(\boldsymbol{J}_e - \overline{\boldsymbol{J}} \tfrac{|\boldsymbol{v}|^2}{2} + \boldsymbol{T}^{\perp}\boldsymbol{v} + (\boldsymbol{v} \otimes \overline{\boldsymbol{J}})\boldsymbol{v} + \boldsymbol{J}_{\varphi}\mu \Big) \\
&\quad + \nabla \cdot \Big(- \delta\gamma'(g(c^{(2)}))\boldsymbol{J}_{\Gamma} - \sum_{i=1,2} \xi_i G_i'(c^{(i)})\boldsymbol{J}_c^{(i)} + \mathcal{W}\varepsilon\sigma(g)\nabla\varphi\partial_t^{\bullet}\varphi \Big) \\
&\quad + \delta\boldsymbol{J}_{\Gamma} \cdot \nabla\gamma'(g(c^{(2)})) + \sum_{i=1,2} \xi_i \boldsymbol{J}_c^{(i)} \cdot \nabla G_i'(c^{(i)}) + \boldsymbol{J}_{\varphi} \cdot \nabla\mu - \delta j_1(\gamma'(g(c^{(2)})) - G_1'(c^{(1)})) \\
&\quad + \nabla\boldsymbol{v} \colon \Big(\delta\sigma(g) + \xi_1(G_1(c^{(1)}) - G_1'(c^{(1)})c^{(1)}) + \xi_2(G_2(c^{(2)}) - G_2'(c^{(2)})c^{(2)}) \Big)\boldsymbol{I} \\
&\quad - \nabla\boldsymbol{v} \colon (\boldsymbol{T} + \boldsymbol{v} \otimes \overline{\boldsymbol{J}} + \mathcal{W}\varepsilon\sigma(g)\nabla\varphi \otimes \nabla\varphi + \varphi\mu\boldsymbol{I}).
\end{aligned}$$

We choose $\boldsymbol{J}_e$ so that the divergence term in the calculation of $-\mathcal{D}$ cancels, $\boldsymbol{T}$ as in (3.2.12) with $\sigma(g)$, $\boldsymbol{J}_{\varphi}$ as in (3.2.11), and $\boldsymbol{J}_c^{(i)}$ as in (3.2.9). Furthermore, we choose

$$\boldsymbol{J}_{\Gamma} = -M_{\Gamma}(g(c^{(2)}))\nabla\gamma'(g(c^{(2)})) = -M_{\Gamma}(g(c^{(2)}))\nabla G_2'(c^{(2)}), \tag{3.3.4}$$

$$j_1 = \frac{1}{\alpha^{(1)}}(\gamma'(g(c^{(2)})) - G_1'(c^{(1)})) = \frac{1}{\alpha^{(1)}}(G_2'(c^{(2)}) - G_1'(c^{(1)})). \tag{3.3.5}$$

Then we obtain the energy inequality

$$\begin{aligned}
-\mathcal{D} = &- 2\eta(\varphi)\left|D(\boldsymbol{v})\right|^2 - m(\varphi)\left|\nabla\mu\right|^2 - \sum_{i=1,2} M_c^{(i)}(c^{(i)})\xi_i(\varphi)\left|\nabla G_i'(c^{(i)})\right|^2 \\
&- \delta(\varphi, \nabla\varphi)M_{\Gamma}(g(c^{(2)}))\left|\nabla G_2'(c^{(2)})\right|^2 - \frac{1}{\alpha^{(1)}}\delta(\varphi, \nabla\varphi)\left|G_2'(c^{(2)}) - G_1'(c^{(1)})\right|^2 \leq 0.
\end{aligned}$$

From (3.1.13), (3.1.14), (3.1.15), and (3.3.2) with (3.2.9), (3.2.11), (3.2.12), (3.3.3), (3.3.4), and (3.3.5), the diffuse interface model for case where we have one-sided instantaneous adsorption and one-sided non-instantaneous adsorption (denoted Model B) is

$$\nabla \cdot \boldsymbol{v} = 0, \tag{3.3.6}$$

$$\begin{aligned}
\partial_t(\rho\boldsymbol{v}) + \nabla \cdot (\rho\boldsymbol{v} \otimes \boldsymbol{v}) &= \nabla \cdot \Big(-p\boldsymbol{I} + 2\eta(\varphi)D(\boldsymbol{v}) + \boldsymbol{v} \otimes \tfrac{\overline{\rho}^{(2)} - \overline{\rho}^{(1)}}{2} m(\varphi)\nabla\mu \Big) \\
&\quad + \nabla \cdot \big(\sigma(g)(\delta\boldsymbol{I} - \mathcal{W}\varepsilon\nabla\varphi \otimes \nabla\varphi) \big),
\end{aligned} \tag{3.3.7}$$

$$\partial_t^{\bullet}\varphi = \nabla \cdot (m(\varphi)\nabla\mu), \tag{3.3.8}$$

$$\mu = -\nabla \cdot (\mathcal{W}\varepsilon\sigma(g)\nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\sigma(g)W'(\varphi), \tag{3.3.9}$$

$$+\sum_{i=1,2}\xi_i'(\varphi)(G_i(c^{(i)})-G_i'(c^{(i)})c^{(i)}) \tag{3.3.10}$$

$$\begin{aligned}\partial_t^\bullet(\xi_1 c^{(1)}) &= \nabla\cdot(M_c^{(1)}(c^{(1)})\xi_1\nabla G_1'(c^{(1)})) \\ &\quad+\frac{1}{\alpha^{(1)}}\delta(G_2'(c^{(2)})-G_1'(c^{(1)})),\end{aligned} \tag{3.3.11}$$

$$\begin{aligned}\partial_t^\bullet(\xi_2 c^{(2)}+\delta g(c^{(2)})) &= \nabla\cdot(M_c^{(2)}(c^{(2)})\xi_2\nabla G_2'(c^{(2)})) \\ &\quad+\nabla\cdot(M_\Gamma(g(c^{(2)}))\delta\nabla G_2'(c^{(2)}))-\frac{1}{\alpha^{(1)}}\delta(G_2'(c^{(2)})-G_1'(c^{(1)})).\end{aligned} \tag{3.3.12}$$

3.4 Instantaneous adsorption, two-sided (Model C)

We now derive a model for instantaneous adsorption that is two-sided. Since we assume local thermodynamical equilibrium, the chemical potentials $G_1'(c^{(1)})$, $G_2'(c^{(2)})$ and $\gamma'(c^\Gamma)$ are equal on the interface. We therefore introduce a chemical potential, denoted by q, and consider this as an unknown field rather than the densities of the surfactants. By Assumption P6, the chemical potentials G_i' and γ' are strictly monotone and we obtain a one-to-one correspondence between the $c^{(i)}$ and q, i.e.,

$$c^{(1)}=(G_1')^{-1}(q),\quad c^{(2)}=(G_2')^{-1}(q),\quad c^\Gamma=(\gamma')^{-1}(q).$$

We then also may write the surface tension as a function of q,

$$\tilde\sigma(q)=\sigma(c^\Gamma(q))=\gamma(c^\Gamma(q))-c^\Gamma(q)q.$$

Summing (3.2.3) for $i=1,2$ and (3.2.4) we obtain the equation for surfactants as follows:

$$\partial_t^\bullet\left(\sum_{i=1,2}\xi_i(\varphi)c^{(i)}(q)+\delta(\varphi,\nabla\varphi)c^\Gamma(q)\right)=-\nabla\cdot\left(\sum_{i=1,2}\xi_i(\varphi)\boldsymbol{J}_c^{(i)}+\delta(\varphi,\nabla\varphi)\boldsymbol{J}_\Gamma\right). \tag{3.4.1}$$

The energy density of the system is given by

$$e(\varphi,\nabla\varphi,\boldsymbol{v},q)=\frac{1}{2}\rho\left|\boldsymbol{v}\right|^2+\sum_{i=1,2}\xi_i(\varphi)G_i(c^{(i)}(q))+\delta(\varphi,\nabla\varphi)\gamma(c^\Gamma(q)),$$

and similar computations as in the previous models yield

$$\begin{aligned}-\mathcal{D}=\nabla\cdot(\boldsymbol{J}_e-\overline{\boldsymbol{J}}\tfrac{|\boldsymbol{v}|^2}{2}+(\boldsymbol{v}\otimes\overline{\boldsymbol{J}})\boldsymbol{v}-\delta q\boldsymbol{J}_\Gamma-\xi_1 q\boldsymbol{J}_c^{(1)}-\xi_2 q\boldsymbol{J}_c^{(2)}+\mathcal{W}\varepsilon\tilde\sigma(q)\nabla\varphi\partial_t^\bullet\varphi)\\+\nabla\cdot\left(\boldsymbol{T}^\perp\boldsymbol{v}+\boldsymbol{J}_\varphi\mu\right)+\boldsymbol{J}_\varphi\cdot\nabla\mu+\delta\boldsymbol{J}_\Gamma\cdot\nabla q+\xi_1(\varphi)\boldsymbol{J}_c^{(1)}\cdot\nabla q+\xi_2(\varphi)\boldsymbol{J}_c^{(2)}\cdot\nabla q\end{aligned}$$

$$
\begin{aligned}
&- \nabla \boldsymbol{v} \colon (\boldsymbol{T} + \boldsymbol{v} \otimes \overline{\boldsymbol{J}} + \mathcal{W}\varepsilon\tilde{\sigma}(q)\nabla\varphi \otimes \nabla\varphi) \\
&+ \nabla \boldsymbol{v} \colon \boldsymbol{I}\Big(\varphi\mu - \delta\tilde{\sigma}(q) - \sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}(q)) - qc^{(i)}(q))\Big),
\end{aligned}
$$

where

$$
\mu = \sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}(q)) - qc^{(i)}(q)) - \nabla \cdot (\mathcal{W}\varepsilon\tilde{\sigma}(q)\nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\tilde{\sigma}(q)W'(\varphi). \quad (3.4.2)
$$

Choosing $\boldsymbol{J}_e$ so that the divergence term in the calculation of $-\mathcal{D}$ cancels, $\boldsymbol{T}$ as in (3.2.12) with $\tilde{\sigma}(q)$, $\boldsymbol{J}_\varphi$ as in (3.2.11), and setting

$$
\boldsymbol{J}_c^{(i)} = -M_c^{(i)}(c^{(i)}(q))\nabla q, \quad \boldsymbol{J}_\Gamma = -M_\Gamma(c^\Gamma(q))\nabla q, \quad (3.4.3)
$$

leads to the following energy inequality:

$$
\begin{aligned}
-\mathcal{D} = &-2\eta(\varphi)\,|D(\boldsymbol{v})|^2 - m(\varphi)\,|\nabla\mu|^2 \\
&- \Big(\sum_{i=1,2} M_c^{(i)}(c^{(i)}(q))\xi_i(\varphi) + M_\Gamma(c^\Gamma(q))\delta(\varphi, \nabla\varphi)\Big)\,|\nabla q|^2 \le 0.
\end{aligned}
$$

From (3.1.13), (3.1.14), (3.1.15), and (3.4.1) with (3.2.11), (3.2.12), (3.4.2), and (3.4.3), the diffuse interface model for this case of instantaneous adsorption based on the chemical potential as a field (denoted Model C) is

$$
\begin{aligned}
\nabla \cdot \boldsymbol{v} &= 0, && (3.4.4)\\
\partial_t(\rho\boldsymbol{v}) + \nabla \cdot (\rho\boldsymbol{v} \otimes \boldsymbol{v} + p\boldsymbol{I} - 2\eta(\varphi)D(\boldsymbol{v})) &= \nabla \cdot \Big(\boldsymbol{v} \otimes \tfrac{\overline{\rho}^{(2)} - \overline{\rho}^{(1)}}{2} m(\varphi)\nabla\mu\Big) && (3.4.5)\\
&\quad + \nabla \cdot \big(\tilde{\sigma}(q)(\delta\boldsymbol{I} - \mathcal{W}\varepsilon\nabla\varphi \otimes \nabla\varphi)\big), \\
\partial_t^\bullet \varphi &= \nabla \cdot (m(\varphi)\nabla\mu), && (3.4.6)\\
\mu + \nabla \cdot (\mathcal{W}\varepsilon\tilde{\sigma}(q)\nabla\varphi) - \frac{\mathcal{W}}{\varepsilon}\tilde{\sigma}(q)W'(\varphi) &= \sum_{i=1,2} \xi_i'(\varphi)(G(c^{(i)}) - qc^{(i)}), && (3.4.7)\\
\partial_t^\bullet\big(\xi_1 c^{(1)}(q) + \xi_2 c^{(2)}(q) + \delta c^\Gamma(q)\big) &= \sum_{i=1,2} \nabla \cdot \big(M_c^{(i)}(c^{(i)}(q))\xi_i\nabla q\big) && (3.4.8)\\
&\quad + \nabla \cdot \big(M_\Gamma(c^\Gamma(q))\delta\nabla q\big).
\end{aligned}
$$

3.5 Specific models

3.5.1 Insoluble surfactants

Similar as in Section 2.4.3, we can consider a phase field model for insoluble surfactants. The resulting model is a system for the unknowns $\boldsymbol{v}$, p, φ, μ, c^Γ and is obtained by omitting (3.2.17) and dropping the last term in (3.2.16) and in (3.2.18). Formally, we set $\xi_i \equiv 0$ and $\frac{1}{\alpha^{(i)}} = 0$ in (3.2.13) – (3.2.18).

3.5.2 Mobility for the phase field equation

We will choose the functional form of the mobility to be

$$m(\varphi) = m_1(1-\varphi^2)_+, \tag{3.5.1}$$

where $m_1 > 0$ is a constant and $(\cdot)_+$ denotes the positive part of the quantity in the brackets. This degenerate mobility switches off diffusion in the bulk phases away from the interfacial layer. In this case, the phase field equations (3.2.15), (3.2.16) lead to a pure advection of the interface. We remark that the choice $m(\varphi) = \varepsilon m_1$ also leads to a pure advection of the interface, while a constant mobility $m(\varphi) = m_1$ leads to interface conditions similar to the ones in the Mullins–Sekerka model; see Abels, Garcke, and Grün [2011] for more details.

3.5.3 Diffusivities

If we set

$$M_c^{(i)} = D_c^{(i)} \frac{1}{G_i''(c^{(i)})}, \quad M_\Gamma(c^\Gamma) = D_\Gamma \frac{1}{\gamma''(c^\Gamma)},$$

for constants $D_c^{(i)}$ and D_Γ, then we derive Fick's law for the surfactant

$$\boldsymbol{J}_c^{(i)} = -D_c^{(i)} \nabla c^{(i)}, \quad \boldsymbol{J}_\Gamma = -D_\Gamma \nabla c^\Gamma.$$

3.5.4 Partial linearisation

Depending on the isotherm and the constitutive assumptions on the fluxes it may be possible to rewrite (3.4.8) so that it is better amenable to numerical simulations. For instance, the Henry isotherm implies that $c^{(1)}$, $c^{(2)}$, and c^Γ are multiples of each other (see Table 2.1), say $c^{(i)} = \beta^{(i)} c$, $c^\Gamma = \beta^\Gamma c$, $i = 1, 2$, for some field c defined on the whole domain Ω. If we further assume Fick's law for the fluxes as above in

Section 3.5.3 with constants $\tilde{D}_c^{(i)}$ and $\tilde{D}_\Gamma$, then we can express (3.4.8) as a linear equation in c:

$$\partial_t^\bullet \left(\left(\beta^{(1)}\xi_1 + \beta^{(2)}\xi_2 + \beta^\Gamma \delta \right) c \right) = \nabla \cdot \left(\left(\tilde{D}_c^{(1)}\xi_1 + \tilde{D}_c^{(2)}\xi_2 + \tilde{D}_\Gamma \delta \right) \nabla c \right).$$

3.5.5 Obstacle potential

If W is chosen to be a potential of double-obstacle type, i.e., $W(\varphi) = F(\varphi) + I_{[-1,1]}(\varphi)$ with $F(\pm 1) = 0$, then equation (3.2.16) is formulated as the following variational inequality: For all $\psi \in \mathcal{K} := \{\eta \in H^1(\Omega) : |\eta| \leq 1\}$,

$$\begin{aligned} &\int_\Omega -\mu(\psi - \varphi) + \mathcal{W}\varepsilon\sigma(c^\Gamma)\nabla\varphi \cdot (\nabla\psi - \nabla\varphi) + \frac{\mathcal{W}}{\varepsilon}\sigma(c^\Gamma)F'(\varphi)(\psi - \varphi) \\ &+ \int_\Omega \sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)})(\psi - \varphi) \geq 0. \end{aligned} \tag{3.5.2}$$

3.5.6 Reformulation of the momentum equation

A short computation shows that

$$\begin{aligned} \mu\nabla\varphi = \nabla \cdot (\sigma(\delta(\varphi, \nabla\varphi)\boldsymbol{I} - \mathcal{W}\varepsilon\nabla\varphi \otimes \nabla\varphi)) - \delta(\varphi, \nabla\varphi)\nabla\sigma \\ + \sum_{i=1,2} \xi_i'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)})\nabla\varphi. \end{aligned}$$

Hence the momentum equation (3.2.14) can be reformulated as

$$\begin{aligned} \partial_t(\rho\boldsymbol{v}) + \nabla \cdot (\rho\boldsymbol{v} \otimes \boldsymbol{v}) = \nabla \cdot \Big(-p\boldsymbol{I} + 2\eta(\varphi)D(\boldsymbol{v}) + \boldsymbol{v} \otimes \tfrac{\overline{\rho}^{(2)} - \overline{\rho}^{(1)}}{2} m(\varphi)\nabla\mu \Big) \\ + \mu\nabla\varphi + \delta(\varphi, \nabla\varphi)\nabla\sigma - \sum_{i=1,2} \xi'(\varphi)(G_i(c^{(i)}) - G_i'(c^{(i)})c^{(i)})\nabla\varphi. \end{aligned}$$

3.5.7 Non-dimensional evolution equations

We consider the following dimensionless variables:

$$\delta_* = L\delta,\ \varepsilon_* = \frac{\varepsilon}{L},\ m_* = \frac{m(\varphi)\Sigma T}{L^3},\ \mu_* = \frac{\mu L}{\Sigma}$$

with the characteristic length L, the scale Σ for the surface tension and a characteristic time T. In addition, we scale the bulk densities by L^3 and the interfacial density by L^2. The dimensionless density and viscosity are

$$\rho_* = \rho/\overline{\rho}^{(2)} = u_1\lambda_\rho + u_2, \quad \eta_* = \eta/\eta^{(2)} = u_1\lambda_\eta + u_2$$

where $\lambda_\rho = \overline{\rho}^{(1)}/\overline{\rho}^{(2)}$, $\lambda_\eta = \eta^{(1)}/\eta^{(2)}$ are the density and viscosity ratios. Set $\mathrm{Re} = (\overline{\rho}^{(2)}L^2)/(T\eta^{(2)})$, $\mathrm{Ca} = (\eta^{(2)}L)/(T\Sigma)$ to be the Reynolds and capillary numbers respectively. Then the dimensionless fluid equations are

$$\nabla_* \cdot \boldsymbol{v}_* = 0, \tag{3.5.3}$$

$$\begin{aligned}\partial_{t_*}(\rho_*\boldsymbol{v}_*) + \nabla_* \cdot (\rho_*\boldsymbol{v}_* \otimes \boldsymbol{v}_*) = \nabla_* \cdot \Big(- p_*\boldsymbol{I} + \frac{2\eta_*}{\mathrm{Re}} D(\boldsymbol{v}_*) + \boldsymbol{v}_* \otimes \frac{1-\lambda_\rho}{2} m_*(\varphi)\nabla_*\mu_*\Big) \\ + \frac{1}{\mathrm{ReCa}} \nabla_* \cdot \big(\sigma_*(\delta_*\boldsymbol{I} - \mathcal{W}\varepsilon_*\nabla_*\varphi \otimes \nabla_*\varphi)\big),\end{aligned} \tag{3.5.4}$$

where $p_* = (pT^2)/(L^2\overline{\rho}^{(2)})$ is the rescaled pressure. The reformulated momentum equation from Section 3.5.6 has the dimensionless form

$$\begin{aligned}\partial_{t_*}(\rho_*\boldsymbol{v}_*) + \nabla_* \cdot (\rho_*\boldsymbol{v}_* \otimes \boldsymbol{v}_*) = \nabla_* \cdot \Big(- p_*\boldsymbol{I} + \frac{2\eta_*}{\mathrm{Re}} D(\boldsymbol{v}_*) + \boldsymbol{v}_* \otimes \frac{1-\lambda_\rho}{2} m_*(\varphi)\nabla_*\mu_*\Big) \\ + \frac{1}{\mathrm{ReCa}}\Big(\mu_*\nabla_*\varphi + \delta_*\nabla_*\sigma_*\Big) \\ - \frac{1}{\mathrm{ReCa}}\Big(\sum_{i=1,2} \xi_i'(\varphi)(G_{i,*}(c_*^{(i)}) - G_{i,*}'(c_*^{(i)})c_*^{(i)})\nabla_*\varphi_*\Big).\end{aligned} \tag{3.5.5}$$

The dimensionless phase field equations are

$$\partial_{t_*}^\bullet \varphi = \nabla_* \cdot (m_*(\varphi)\nabla_*\mu_*), \tag{3.5.6}$$

$$\mu_* = -\nabla_* \cdot (\mathcal{W}\varepsilon_*\sigma_*\nabla_*\varphi) + \frac{\mathcal{W}}{\varepsilon_*}\sigma_* W'(\varphi) + \sum_{i=1,2} \xi_i'(\varphi)(G_{*,i}(c_*^{(i)}) - G_{*,i}'(c_*^{(i)})c_*^{(i)}), \tag{3.5.7}$$

The dimensionless surfactant equations for Model A are

$$\partial_{t_*}^\bullet(\xi_i c_*^{(i)}) - \nabla_* \cdot \Big(M_{c,*}^{(i)}\xi_i\nabla_* G_{i,*}'(c_*^{(i)})\Big) = \frac{1}{\alpha_*^{(i)}}\delta_*(\gamma_*'(c_*^\Gamma) - G_{i,*}'(c_*^{(i)})), \tag{3.5.8}$$

$$\partial_{t_*}^\bullet(\delta_* c_*^\Gamma) - \nabla_* \cdot \Big(M_{\Gamma,*}\delta_*\nabla_*\gamma_*'(c_*^\Gamma)\Big) = -\delta_* \sum_{i=1,2} \frac{1}{\alpha_*^{(i)}}(\gamma_*'(c_*^\Gamma) - G_{*,i}'(c_*^{(i)})). \tag{3.5.9}$$

For Model B, the dimensionless surfactant equations read

$$\begin{aligned}&\partial_{t_*}^\bullet\big(\xi_1 c_*^{(1)}\big) - \nabla_* \cdot \Big(M_{c,*}^{(1)}\xi_1\nabla_* G_{1,*}'(c_*^{(1)})\Big) = j_{1,*}, \\ &\partial_{t_*}^\bullet\big(\xi_2 c_* + \delta_* g_*\big) - \nabla_* \cdot \Big(M_{c,*}^{(2)}\xi_2\nabla_* G_{2,*}'(c_*^{(2)}) + M_{\Gamma,*}\delta_*\nabla_* G_{2,*}'(c_*^{(2)})\Big) = -j_{1,*},\end{aligned}$$

with $j_{1,*} = \frac{1}{\alpha_*^{(1)}}\delta_*(G'_{2,*}(c_*^{(2)}) - G'_{1,*}(c_*^{(1)}))$. For Model C, it reads as

$$\partial_{t_*}^{\bullet}\left(\xi_1 c_*^{(1)}(q_*) + \xi_2 c_*^{(2)}(q_*) + \delta_* c_*^{\Gamma}(q_*)\right) - \nabla_* \cdot \left(M_{c,*}^{(1)}\xi_1\nabla_* q_* + M_{c,*}^{(2)}\xi_2\nabla_* q_* + M_{\Gamma,*}\delta_*\nabla_* q_*\right) = 0. \tag{3.5.10}$$

If we consider the mobilities in Section 3.5.3, the dimensionless surfactant equations for Model A are

$$\partial_{t_*}^{\bullet}(\xi_i c_*^{(i)}) - \nabla_* \cdot \left(\frac{1}{\mathrm{Pe}_{c,i}}\xi_i\nabla_* c_*^{(i)}\right) = \frac{1}{\alpha_*^{(i)}}\delta_*(\gamma'_*(c_*^{\Gamma}) - G'_{*,i}(c_*^{(i)})), \tag{3.5.11}$$

$$\partial_{t_*}^{\bullet}(\delta_* c_*^{\Gamma}) - \nabla_* \cdot \left(\frac{1}{\mathrm{Pe}_{\Gamma}}\delta_*\nabla_* c_*^{\Gamma}\right) = -\delta_* \sum_{i=1,2}\frac{1}{\alpha_*^{(i)}}(\gamma'_*(c_*^{\Gamma}) - G'_{*,i}(c_*^{(i)})). \tag{3.5.12}$$

For Model B, the dimensionless surfactant equations with Fickian diffusion read

$$\partial_{t_*}^{\bullet}\left(\xi_1 c_*^{(1)}\right) - \nabla_* \cdot \left(\frac{1}{\mathrm{Pe}_{c,1}}\xi_1\nabla_* c_*\right) = j_{1,*}, \tag{3.5.13}$$

$$\partial_{t_*}^{\bullet}\left(\xi_2 c_*^{(2)} + \delta_* g_*\right) - \nabla_* \cdot \left(\frac{1}{\mathrm{Pe}_{c,2}}\xi_2\nabla_* c_*^{(2)} + \frac{1}{\mathrm{Pe}_{\Gamma}}\delta_*\nabla_* c_*^{(2)}\right) = -j_{1,*}. \tag{3.5.14}$$

Chapter 4

Sharp interface asymptotics

4.1 Formal asymptotic analysis

In this section we identify the sharp interface limit of the diffuse interface models introduced in the previous section by the method of matching formal asymptotic expansions. We will apply this method to Model A, where we distinguish two different scalings of $\alpha^{(i)}$, namely $\mathcal{O}(1)$ and $\mathcal{O}(\varepsilon)$. We briefly outline the procedure for Models B and C. We remark that in the subsequent asymptotic analysis, some orders of the expansions will yield the trivial statement $0 = 0$. If so, we will neglect these and look at the next order of the expansions.

4.1.1 Outer expansions, equations, and solutions

We assume there exist the following asymptotic expansions in ε for $u_\varepsilon = u(t, \boldsymbol{x}; \varepsilon) \in \{\boldsymbol{v}_\varepsilon, p_\varepsilon, \varphi_\varepsilon, \mu_\varepsilon, c_\varepsilon^{(i)}, c_\varepsilon^\Gamma\}$ in the bulk regions away from the interface:

$$u_\varepsilon(t, \boldsymbol{x}) = u(t, \boldsymbol{x}; \varepsilon) = u_0(t, \boldsymbol{x}) + \varepsilon u_1(t, \boldsymbol{x}) + \mathcal{O}(\varepsilon^2). \tag{4.1.1}$$

Substituting these expansions into Model A and (3.2.16) to order -1 gives

$$0 = \mathcal{W}\sigma(c_0^\Gamma)W'(\varphi_0).$$

As $\sigma(\cdot) > 0$, we obtain the identity $W'(\varphi_0) = 0$. But the only stable solutions to this equation are the minima of $W(\cdot)$, hence $\varphi_0 = \pm 1$. We denote $\Omega^{(2)}$ and $\Omega^{(1)}$ to be the sets where $\varphi_0 = 1$ and $\varphi_0 = -1$ respectively. Immediately, from (3.2.1), we see that

$$\delta(\varphi_0, \nabla\varphi_0) = 0,$$

so that (3.2.18) fully degenerates in both domains $\Omega^{(2)}$ and $\Omega^{(1)}$, whence c_0^Γ remains undetermined in the bulk. Similarly, μ_0 is undetermined in the bulk due to $m(\varphi_0) = 0$ (recall (3.5.1)). Moreover, the fluxes $\delta \boldsymbol{J}_\Gamma = -M_\Gamma(c^\Gamma)\delta\nabla\gamma'(c^\Gamma)$ and $\boldsymbol{J}_\varphi = -m(\varphi)\nabla\varphi$ vanish in both domains

The zeroth order expansions of the fluid equations yield

$$\begin{aligned} \nabla \cdot \boldsymbol{v}_0 &= 0, \\ \partial_t(\overline{\rho}^{(i)}\boldsymbol{v}_0) + \nabla \cdot (\overline{\rho}^{(i)}\boldsymbol{v}_0 \otimes \boldsymbol{v}_0 - 2\eta^{(i)}D(\boldsymbol{v}_0) + p_0\boldsymbol{I}) &= 0. \end{aligned}$$

The bulk surfactant equation gives, to the zeroth order,

$$\partial_t(\xi_i(\varphi_0)c_0^{(i)}) + \boldsymbol{v}_0 \cdot \nabla(\xi_i(\varphi_0)c_0^{(i)}) - \nabla \cdot (\xi_i(\varphi_0)M_i(c_0^{(i)})\nabla G_i'(c_0^{(i)})) = 0, \quad i = 1, 2.$$

By the definition of $\xi_i(\varphi)$, we have

$$\xi_1(-1) = 1, \quad \xi_1(+1) = 0, \quad \xi_2(-1) = 0, \quad \xi_2(+1) = 1, \tag{4.1.2}$$

and so, we obtain

$$\begin{aligned} \partial_t c_0^{(1)} + \boldsymbol{v}_0 \cdot \nabla c_0^{(1)} - \nabla \cdot (M_1(c_0^{(1)})\nabla G_1'(c_0^{(1)})) &= 0, \text{ in } \Omega^{(1)}, \\ \partial_t c_0^{(2)} + \boldsymbol{v}_0 \cdot \nabla c_0^{(2)} - \nabla \cdot (M_2(c_0^{(2)})\nabla G_2'(c_0^{(2)})) &= 0, \text{ in } \Omega^{(2)}. \end{aligned}$$

Moreover, we note that $\xi_1 \boldsymbol{J}_c^{(1)} = -\xi_1 M_c^{(1)}\nabla G_1'(c^{(1)})$ vanishes in $\Omega^{(2)}$, while $\xi_2 \boldsymbol{J}_c^{(2)} = -\xi_2 M_c^{(2)}\nabla G_2'(c^{(2)})$ vanishes in $\Omega^{(1)}$.

For the double-obstacle potential, equation (3.2.16) is replaced by (3.5.2) which, to order -1, is the variational inequality

$$-\int_\Omega \sigma(c_0^\Gamma)\varphi_0(\psi_0 - \varphi_0) \geq 0, \quad \forall \psi_0 \in \mathcal{K}.$$

Since $\sigma > 0$, this implies that φ_0 must take the values ± 1 and we can define sets $\Omega^{(2)}, \Omega^{(1)}$ as in the case with the double-well potential.

4.1.2 Inner expansions and matching conditions

Let us assume that the zero level sets of φ_ε converge to some hypersurface Γ moving with a normal velocity denoted by u_Γ as $\varepsilon \to 0$. Close to Γ, we denote by $d(t, \boldsymbol{x})$ the signed distance function of a point $\boldsymbol{x} \in \Omega$ to Γ with the convention $d(t, \boldsymbol{x}) > 0$ if $x \in \Omega^{(2)}(t)$, and set $z(t, \boldsymbol{x}) = d(t, \boldsymbol{x})/\varepsilon$. We write each field $u(t, \boldsymbol{x})$ close to Γ in new coordinates $U(t, s, z)$, where s are tangential spatial coordinates on Γ. The upshot

is

$$\partial_t u = -\frac{1}{\varepsilon} u_\Gamma \partial_z U + \partial_t^\circ U + \text{ h.o.t.},$$
$$\nabla_{\boldsymbol{x}} u = \frac{1}{\varepsilon} \partial_z U \boldsymbol{\nu} + \nabla_\Gamma U + \text{ h.o.t.},$$

where $\boldsymbol{\nu} = \nabla_{\boldsymbol{x}} d$ is the unit normal pointing into $\Omega^{(2)}$, $\partial_t^\circ(\cdot) = \partial_t(\cdot) + u_\Gamma \boldsymbol{\nu} \cdot \nabla_{\boldsymbol{x}}(\cdot)$ is the normal time derivative, ∇_Γ is the spatial surface gradient on Γ, and h.o.t. denotes higher order terms (see the appendix of Abels, Garcke, and Grün [2011] for a proof).

We assume that the inner expansions of unknown fields $u \in \{\boldsymbol{v}_\varepsilon, p_\varepsilon, \varphi_\varepsilon, \mu_\varepsilon, c_\varepsilon^{(i)}, c_\varepsilon^\Gamma\}$ take the form

$$u(t, \boldsymbol{x}; \varepsilon) = U(t, s, z; \varepsilon) = U_0(t, s, z) + \varepsilon U_1(t, s, z) + \mathcal{O}(\varepsilon^2)$$

with inner variables $U \in \{\boldsymbol{V}, P, \Phi, M, C^{(i)}, C^\Gamma\}$. The assumption that the zero level sets of φ_ε converge to Γ implies that Φ satisfies

$$\Phi_0(t, s, 0) = 0.$$

Regarding the double-obstacle potential, we further assume that Φ is monotone increasing with z and the interfacial layer has finite thickness of $2l$, where the value of l will come out of the asymptotic analysis (see Blowey and Elliott [1993]). For the double-well potential we take $l = \infty$. Furthermore, we assume that

$$\Phi(t, s, l; \varepsilon) = 1, \quad \Phi(t, s, -l; \varepsilon) = -1. \tag{4.1.3}$$

In order to match the inner expansions valid in the interfacial layers to outer expansions we employ the following matching conditions [Garcke and Stinner, 2006]: As $z \to \pm l$,

$$U_0(t, s, z) \sim u_0^\pm(t, \boldsymbol{x}), \tag{4.1.4}$$
$$\partial_z U_0(t, s, z) \sim 0, \tag{4.1.5}$$
$$\partial_z U_1(t, s, z) \sim \nabla u_0^\pm(t, \boldsymbol{x}) \cdot \boldsymbol{\nu}, \tag{4.1.6}$$
$$\partial_z U_2(t, s, z) \sim \nabla u_1^\pm(t, \boldsymbol{x}) \cdot \boldsymbol{\nu} + \big((\boldsymbol{\nu} \cdot \nabla)(\boldsymbol{\nu} \cdot \nabla) u_0^\pm(t, \boldsymbol{x})\big) z, \tag{4.1.7}$$

where $u_0^\pm$ denotes the limit $\lim_{\delta \searrow 0} u_0(\boldsymbol{x} \pm \delta \boldsymbol{\nu})$ at a point $\boldsymbol{x} \in \Gamma$.

Note that there are no bulk fields if $u = c^\Gamma$ or $u = \mu$. But we have matching

conditions for the fluxes of these quantities, namely

$$\delta \boldsymbol{J}_\Gamma \to \mathbf{0} \text{ and } \boldsymbol{J}_\varphi \to \mathbf{0} \text{ as } z \to \pm l. \tag{4.1.8}$$

Similarly, there are no bulk fields for $c^{(1)}$ in $\Omega^{(2)}$ and $c^{(2)}$ in $\Omega^{(1)}$. So we assume that the fluxes satisfy the matching conditions

$$\xi_1 \boldsymbol{J}_c^{(1)} \to \mathbf{0} \text{ as } z \to +l, \quad \xi_2 \boldsymbol{J}_c^{(2)} \to \mathbf{0} \text{ as } z \to -l. \tag{4.1.9}$$

4.1.3 Asymptotics for Model A

We begin by stating a few expansions of the most complicated terms for later use. These can be obtained by some short calculations. First,

$$\begin{aligned}\varepsilon\nabla\cdot(\sigma(c^\Gamma)\nabla\varphi\otimes\nabla\varphi) &= \frac{1}{\varepsilon^2}\partial_z(\sigma(c^\Gamma)(\partial_z\Phi)^2\boldsymbol{\nu}) + \frac{1}{\varepsilon}\partial_z(\sigma(c^\Gamma)\partial_z\Phi\nabla_\Gamma\Phi)\\ &\quad + \frac{1}{\varepsilon}\nabla_\Gamma\cdot(\sigma(c^\Gamma)(\partial_z\Phi)^2\boldsymbol{\nu}\otimes\boldsymbol{\nu}) + \nabla_\Gamma\cdot(\sigma(c^\Gamma)\partial_z\Phi(\boldsymbol{\nu}\otimes\nabla_\Gamma\Phi + \nabla_\Gamma\Phi\otimes\boldsymbol{\nu})) + \text{ h.o.t.},\end{aligned}$$

where $\nabla_\Gamma\cdot$ of a 2-tensor is the surface divergence applied to each row. Then, setting $\mathcal{E}(\boldsymbol{A}) = \frac{1}{2}(\boldsymbol{A}+\boldsymbol{A}^\perp)$ for a tensor $\boldsymbol{A}$ one can show that

$$\begin{aligned}\nabla\cdot(\eta(\varphi)D(\boldsymbol{v})) &= \frac{1}{\varepsilon^2}\partial_z(\eta(\Phi)\mathcal{E}(\partial_z\boldsymbol{V}\otimes\boldsymbol{\nu})\boldsymbol{\nu})\\ &\quad + \frac{1}{\varepsilon}\partial_z(\eta(\Phi)\mathcal{E}(\nabla_\Gamma\boldsymbol{V})\boldsymbol{\nu}) + \frac{1}{\varepsilon}\nabla_\Gamma\cdot(\eta(\Phi)\mathcal{E}(\partial_z\boldsymbol{V}\otimes\boldsymbol{\nu})) + \text{ h.o.t.}.\end{aligned}$$

Next, observe that

$$\delta(\varphi,\nabla\varphi) = \mathcal{W}\left(\frac{1}{2\varepsilon}|\partial_z\Phi|^2 + \frac{1}{\varepsilon}W(\Phi) + \frac{\varepsilon}{2}|\nabla_\Gamma\Phi|^2 + \text{ h.o.t.}\right),$$

and so the fluxes $\delta\boldsymbol{J}_\Gamma$, $\boldsymbol{J}_\varphi$, and $\xi_i\boldsymbol{J}_c^{(i)}$ expanded in the new coordinates read as

$$\begin{aligned}\delta\boldsymbol{J}_\Gamma &= -\mathcal{W}M_\Gamma(C^\Gamma)\left(\frac{1}{2}|\partial_z\Phi|^2 + W(\Phi)\right)\left(\frac{1}{\varepsilon^2}\partial_z(\gamma'(C^\Gamma))\boldsymbol{\nu} + \frac{1}{\varepsilon}\nabla_\Gamma(\gamma'(C^\Gamma))\right)\\ &\quad - \mathcal{W}M_\Gamma(C^\Gamma)|\nabla_\Gamma\Phi|^2\,\partial_z(\gamma'(C^\Gamma))\boldsymbol{\nu} + \text{ h.o.t.},\\ \boldsymbol{J}_\varphi &= -m(\Phi)\left(\frac{1}{\varepsilon}\partial_z M\boldsymbol{\nu} + \nabla_\Gamma M\right) + \text{ h.o.t.},\\ \xi_i\boldsymbol{J}_c^{(i)} &= -M_c^{(i)}(C^{(i)})\xi_i(\Phi)\left(\frac{1}{\varepsilon}\partial_z(G_i'(C^{(i)}))\boldsymbol{\nu} + \nabla_\Gamma(G_i'(C^{(i)}))\right) + \text{ h.o.t.}.\end{aligned}$$

Inner equations and solutions to leading order

The order -3 terms in (3.2.18) give

$$\mathcal{W}\partial_z(M_\Gamma(C_0^\Gamma)(\tfrac{1}{2}\left|\partial_z\Phi_0\right|^2 + W(\Phi_0))\partial_z\gamma'(C_0^\Gamma)) = 0.$$

Integrating from $-l$ to z and using (4.1.8) yields

$$M_\Gamma(C_0^\Gamma)(\tfrac{1}{2}\left|\partial_z\Phi_0\right|^2 + W(\Phi_0))\partial_z\gamma'(C_0^\Gamma) = 0.$$

We conclude that

$$\partial_z\gamma'(C_0^\Gamma) = 0 \text{ whenever } |\Phi_0| < 1.$$

Since $\gamma'' > 0$, we obtain that

$$\partial_z C_0^\Gamma = 0 \text{ whenever } |\Phi_0| < 1,$$

which means that C_0^Γ is constant across the interfacial layer. Since the surface tension is given by $\sigma(C_0^\Gamma) = \gamma(C_0^\Gamma) - C_0^\Gamma\gamma'(C_0^\Gamma)$, we also obtain

$$\partial_z\sigma(C_0^\Gamma) = 0 \text{ whenever } |\Phi_0| < 1.$$

To order -1 in (3.2.16) we have

$$\mathcal{W}\sigma(C_0^\Gamma)(-\partial_{zz}\Phi_0 + W'(\Phi_0)) = 0.$$

We can choose Φ_0 such that it is independent of s and t and solves

$$-\partial_{zz}\Phi_0 + W'(\Phi_0) = 0, \tag{4.1.10}$$

with $\Phi_0(0) = 0$ and $\Phi_0(\pm l) = \pm 1$. With the double-well potential $W(\varphi) = \frac{1}{4}(1-\varphi^2)^2$ we have the unique solution

$$\Phi_0(z) = \tanh(z/\sqrt{2}),$$

while for the double-obstacle potential, a unique solution to

$$-\partial_{zz}\Phi_0 - \Phi_0 = 0, \quad |\Phi_0| \le 1, \quad \Phi_0(t,s,0) = 0$$

is

$$\Phi_0(z) = \begin{cases} +1, & \text{if } z \geq \frac{\pi}{2}, \\ \sin(z), & \text{if } |z| < \frac{\pi}{2}, \\ -1, & \text{if } z \leq -\frac{\pi}{2}, \end{cases}$$

so that $l = \frac{\pi}{2}$, and from (4.1.3) we deduce that

$$\Phi_1(t, s, \pm\tfrac{\pi}{2}) = 0. \tag{4.1.11}$$

Multiplying (4.1.10) by $\partial_z \Phi_0$, integrating from $-l$ to z and applying matching (4.1.4) and (4.1.5) to Φ_0 yield the equipartition of energy

$$\frac{1}{2} |\partial_z \Phi_0(z)|^2 = W(\Phi_0(z)). \tag{4.1.12}$$

The order -1 term in the mass balance (3.2.13) gives

$$(\partial_z \boldsymbol{V}_0) \cdot \boldsymbol{\nu} = \partial_z (\boldsymbol{V}_0 \cdot \boldsymbol{\nu}) = 0. \tag{4.1.13}$$

Integrating from $-l$ to l and matching (4.1.4) applied to $\boldsymbol{V}_0$ imply that $\boldsymbol{V}_0 \cdot \boldsymbol{\nu}$ is constant in z and

$$\boldsymbol{v}_0^{(2)} \cdot \boldsymbol{\nu} = \lim_{z \to +\infty} \boldsymbol{V}_0 \cdot \boldsymbol{\nu} = \lim_{z \to -\infty} \boldsymbol{V}_0 \cdot \boldsymbol{\nu} = \boldsymbol{v}_0^{(1)} \cdot \boldsymbol{\nu}, \tag{4.1.14}$$

i.e., the normal velocity is continuous across the interface.

Equation (3.2.17) gives to order -2

$$\partial_z (M_i(C_0^{(i)}) \xi_i(\Phi_0) G_i''(C_0^{(i)}) \partial_z C_0^{(i)}) = 0.$$

In the two-sided model, for $i = 2$ we integrate from $-l$ to z and use (4.1.9) to obtain

$$M_2(C_0^{(2)}) \xi_2(\Phi_0(z)) G_2''(C_0^{(2)}) \partial_z C_0^{(2)} = 0$$

as $\xi_2(-1) = 0$. Since $G_2'' > 0$ we have that $\partial_z C_0^{(2)} = 0$. Similarly, for $C_0^{(1)}$ where we integrate from z to $+l$ and use (4.1.9) to obtain

$$M_1(C_0^{(1)}) \xi_1(\Phi_0(z)) G_1''(C_0^{(1)}) \partial_z C_0^{(1)} = 0$$

as $\xi_1(+1) = 0$. Thus $\partial_z C_0^{(1)} = 0$ follows from the same argument. In the case of the one-sided model, we argue as above to obtain $\partial_z C_0 = 0$.

Using (3.5.1), equation (3.2.15) gives to order -2

$$0 = \partial_z(m_1(1-\Phi_0^2)_+\partial_z M_0).$$

Integrating from $-l$ to z and using (4.1.8) gives

$$0 = m_1(1-\Phi_0^2(z))_+\partial_z M_0.$$

For $|\Phi_0| < 1$ we have $\partial_z M_0 = 0$, hence the term $\nabla\cdot(\boldsymbol{v}\otimes\frac{\overline{\rho}^{(2)}-\overline{\rho}^{(1)}}{2}m(\varphi)\nabla\mu)$ plays no part in the order -2 expansion of the momentum equation (3.2.14). To leading order the momentum equation gives

$$\mathbf{0} = 2\partial_z(\eta(\Phi_0)\partial_z\boldsymbol{V}_0). \tag{4.1.15}$$

With the usual trick of integrating with respect to z from $-l$ to a limit denoted by z again and applying (4.1.5) to $\boldsymbol{V}_0$ we obtain that $\eta(\Phi_0)\partial_z\boldsymbol{V}_0 = 0$. Since $\eta > 0$ we conclude that $\partial_z\boldsymbol{V}_0 = 0$ so that, using (4.1.4), the tangential velocity is continuous across the interface:

$$[\boldsymbol{v}_0]_1^2 = 0.$$

Inner equations and solutions to first order

Equation (3.2.13) of the mass balance yields to zeroth order

$$\partial_z\boldsymbol{V}_1\cdot\boldsymbol{\nu} + \nabla_\Gamma\cdot\boldsymbol{V}_0 = 0, \tag{4.1.16}$$

while equation (3.2.15) gives to order -1

$$(-u_\Gamma + \boldsymbol{V}_0\cdot\boldsymbol{\nu})\partial_z\Phi_0 = \partial_z(m_1(1-\Phi_0^2)_+\partial_z M_1),$$

where we used that $\partial_z M_0 = 0$. Integrating from $-l$ to $+l$ and using (4.1.8) yields

$$2(u_\Gamma - \boldsymbol{v}_0\cdot\boldsymbol{\nu}) = [m_1(1-\Phi_0^2)_+\partial_z M_1]_{-l}^{+l} = 0,$$

and we obtain

$$u_\Gamma = \boldsymbol{v}_0\cdot\boldsymbol{\nu}. \tag{4.1.17}$$

Using equipartition of energy (4.1.12), $\partial_z C_0^{(i)} = 0$, and $u_\Gamma = \boldsymbol{v}_0\cdot\boldsymbol{\nu}$, we obtain

from (3.2.17) at order -1

$$2\frac{\mathcal{W}}{\alpha^{(i)}}(\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)}))W(\Phi_0) = -\partial_z(M_i(C_0^{(i)})\xi_i(\Phi_0)\partial_z(G_i''(C_0^{(i)})C_1^{(i)})). \quad (4.1.18)$$

In the two-sided model, for $i = 2$, integrating (4.1.18) from $-l$ to $+l$ and using (4.1.9) and (3.2.2) leads to

$$\begin{aligned} 0 &= [M_2(C_0^{(2)})\xi_2(\Phi_0)G_2''(C_0^{(2)})\partial_z C_1^{(2)}]_{-l}^{+l} + \frac{2\mathcal{W}}{\alpha^{(2)}}\int_{-l}^{+l}(\gamma'(C_0^\Gamma) - G_2'(C_0^{(2)}))W(\Phi_0)dz \\ &= M_c^{(2)}(c_0^{(2)})\nabla G_2'(c_0^{(2)})\cdot\boldsymbol{\nu} + \frac{1}{\alpha^{(2)}}(\gamma'(c_0^\Gamma) - G_2'(c_0^{(2)})). \end{aligned}$$

Proceeding similarly for $i = 1$, we recover the free boundary conditions

$$\begin{aligned} -M_c^{(2)}(c^{(2)})\nabla G_2'(c_0^{(2)})\cdot\boldsymbol{\nu} = \boldsymbol{J}_{c,0}^{(2)}\cdot\boldsymbol{\nu} &= \frac{1}{\alpha^{(2)}}(\gamma'(c_0^\Gamma) - G_2'(c_0^{(2)})), \\ M_c^{(1)}(c^{(1)})\nabla G_1'(c_0^{(1)})\cdot\boldsymbol{\nu} = -\boldsymbol{J}_{c,0}^{(1)}\cdot\boldsymbol{\nu} &= \frac{1}{\alpha^{(1)}}(\gamma'(c_0^\Gamma) - G_1'(c_0^{(1)})). \end{aligned} \quad (4.1.19)$$

The argument for the one-sided model is similar to the above case with $i = 2$.

Using $\partial_z C_0^\Gamma = 0$, $u_\Gamma = \boldsymbol{v_0}\cdot\boldsymbol{\nu}$, and the equipartition of energy, after integrating from $-l$ to z and using (4.1.8), equation (3.2.18) gives to order -2

$$2\mathcal{W}M_\Gamma(C_0^\Gamma)W(\Phi_0(z))\gamma''(C_0^\Gamma)\partial_z C_1^\Gamma = 0.$$

Since $\gamma'' > 0$ we have that

$$\partial_z C_1^\Gamma = 0 \text{ whenever } |\Phi_0| < 1.$$

Equation (3.2.16) for the chemical potential gives to zeroth order

$$\begin{aligned} M_0 = \mathcal{W}\sigma(C_0^\Gamma)(-\partial_{zz}\Phi_1 + W''(\Phi_0)\Phi_1) + \mathcal{W}\sigma'(C_0^\Gamma)C_1^\Gamma\underbrace{(-\partial_{zz}\Phi_0 + W'(\Phi_0))}_{=0} \\ - \mathcal{W}\nabla_\Gamma\cdot(\sigma(C_0^\Gamma)\boldsymbol{\nu})\partial_z\Phi_0 + \sum_{i=1,2}\xi_i'(\Phi_0)(G_i(C_0^{(i)}) - G_i'(C_0^{(i)})C_0^{(i)}). \end{aligned}$$

To obtain a solution Φ_1, a solvability condition has to hold. Multiplying the above

by $\partial_z\Phi_0$ and integrating from $-l$ to $+l$ gives

$$\int_{-l}^{+l} M_0\partial_z\Phi_0 dz - \int_{-l}^{+l}\sum_{i=1,2}\xi_i'(\Phi_0)(G_i(C_0^{(i)}) - G_i'(C_0^{(i)})C_0^{(i)})\partial_z\Phi_0 dz$$
$$= \mathcal{W}\int_{-l}^{+l}\sigma(C_0^\Gamma)(-\partial_{zz}\Phi_1\partial_z\Phi_0 + W''(\Phi_0)\Phi_1\partial_z\Phi_0) - \nabla_\Gamma\cdot(\sigma(C_0^\Gamma)\boldsymbol{\nu})(\partial_z\Phi_0)^2 dz$$

Integrating by parts, using $\partial_z C_0^{(i)} = 0, \partial_z C_0^\Gamma = 0$, equipartition of energy (4.1.12), and matching lead to

$$2\mu_0 - \sum_{i=1,2}[(G_i(C_0^{(i)}) - G_i'(C_0^{(i)})C_0^{(i)})\xi_i(\Phi_0)]_{-l}^{+l} + \nabla_\Gamma\cdot(\sigma(c_0^\Gamma)\boldsymbol{\nu})$$
$$= \mathcal{W}\left(\int_{-l}^{+l}\sigma(C_0^\Gamma)\underbrace{(\partial_{zz}\Phi_0 - W'(\Phi_0))}_{=0}\partial_z\Phi_1 dz - [\sigma(C_0^\Gamma)(\partial_z\Phi_0\partial_z\Phi_1 - W'(\Phi_0)\Phi_1)]_{-l}^{+l}\right).$$

We use the fact that $W'(\pm1) = 0$ for the double-well potential and (4.1.5) to cancel the jump term. Furthermore

$$\nabla_\Gamma\cdot(\sigma(c_0^\Gamma)\boldsymbol{\nu}) = \sigma(c_0^\Gamma)\nabla_\Gamma\cdot\boldsymbol{\nu} + \underbrace{\nabla_\Gamma\sigma(c_0^\Gamma)\cdot\boldsymbol{\nu}}_{=0} = -\kappa\sigma(c_0^\Gamma),$$

and so we deduce that the solvability condition is

$$2\mu_0 = \sigma(c_0^\Gamma)\kappa + [G_i(c_0^{(i)}) - G_i'(c_0^{(i)})c_0^{(i)}]_1^2. \tag{4.1.20}$$

For the double-obstacle potential, the equation for Φ_1 is expressed as a variational inequality: For all $\psi_0 \in \mathcal{K}$,

$$\mathcal{W}\Big(-\sigma(C_0^\Gamma)(\partial_{zz}\Phi_1 + \Phi_1) - \sigma'(C_0^\Gamma)C_1^\Gamma(\partial_{zz}\Phi_0 + \Phi_0) - \partial_z\Phi_0\nabla_\Gamma\cdot(\sigma(C_0^\Gamma)\boldsymbol{\nu}), \psi_0 - \Phi_0\Big)$$
$$\geq \Big(M_0 - \sum_{i=1,2}\xi_i'(\Phi_0)(G_i(C_0^{(i)}) - G_i'(C_0^{(i)})C_0^{(i)}), \psi_0 - \Phi_0\Big).$$

Whenever $|\Phi_0| < 1$, testing with $\psi_0 = \Phi_0 + \hat{\psi}_0$, with either a non-positive or a non-negative $\hat{\psi}_0$, we obtain the equality

$$-M_0 - \mathcal{W}\sigma(C_0^\Gamma)(\partial_{zz}\Phi_1 + \Phi_1) - \mathcal{W}\sigma'(C_0^\Gamma)C_1^\Gamma(\partial_{zz}\Phi_0 + \Phi_1)$$
$$-\mathcal{W}\partial_z\Phi_0\nabla_\Gamma\cdot(\sigma(C_0^\Gamma)\boldsymbol{\nu}) + \sum_{i=1,2}\xi_i'(\Phi_0)(G_i(C_0^{(i)}) - G_i'(C_0^{(i)})C_0^{(i)}) = 0.$$

Multiplying by $\partial_z \Phi_0$ and integrating from $-l$ to $+l$ gives after matching

$$
\begin{aligned}
&2\mu_0 - \sigma(c_0^\Gamma)\kappa - \sum_{i=1,2} [\xi_i(\varphi_0)(G_i(c_0^{(i)}) - G_i'(c_0^{(i)})c_0^{(i)})]_{-l}^{+l} \\
&= \mathcal{W} \int_{-l}^{+l} -\sigma(C_0^\Gamma)(\partial_{zz}\Phi_1 + \Phi_1)\partial_z\Phi_0 dz \\
&= -\mathcal{W}[\sigma(C_0^\Gamma)(\partial_z\Phi_0\partial_z\Phi_1 + \Phi_0\Phi_1)]_{-l}^{+l} + \mathcal{W}\sigma(C_0^\Gamma) \int_{-l}^{+l} \partial_z\Phi_1(\partial_{zz}\Phi_0 + \Phi_0)dz.
\end{aligned}
$$

The last integral term is zero due to (4.1.10), and using (4.1.5) for Φ_0 and (4.1.11) for Φ_1 at $z = \pm l$ the jump term is also zero. This leads to the same solvability condition as in (4.1.20).

Using $\partial_z M_0 = 0$, $u_\Gamma = \boldsymbol{v}_0 \cdot \boldsymbol{\nu}$, $\nabla_\Gamma \Phi_0 = 0$ and equipartition of energy, the momentum equation (3.2.14) gives to order -1

$$
\begin{aligned}
&\partial_z P_0 \boldsymbol{\nu} - 2\partial_z(\eta(\Phi_0)\mathcal{E}(\partial_z \boldsymbol{V}_1 \otimes \boldsymbol{\nu})\boldsymbol{\nu} + \eta(\Phi_0)\mathcal{E}(\nabla_\Gamma \boldsymbol{V}_0)\boldsymbol{\nu}) \\
&- \partial_z(\boldsymbol{V}_0 \otimes \tfrac{\overline{\rho}^{(2)} - \overline{\rho}^{(1)}}{2} m(\Phi_0)\partial_z M_1 \boldsymbol{\nu}) = \mathcal{W}\,|\partial_z\Phi_0|^2\,(\nabla_\Gamma \cdot (\sigma(C_0^\Gamma)\boldsymbol{I}) - \nabla_\Gamma \cdot (\sigma(C_0^\Gamma)\boldsymbol{\nu} \otimes \boldsymbol{\nu})),
\end{aligned}
$$

where we used that $\boldsymbol{V}_0$ is constant in z. Matching (4.1.6) requires that $\lim_{z\to\pm l} \partial_z \boldsymbol{V}_1 = \nabla \boldsymbol{v}_0^\pm \boldsymbol{\nu}$ and hence

$$
\partial_z \boldsymbol{V}_1 \otimes \boldsymbol{\nu} + \nabla_\Gamma \boldsymbol{V}_0 \to \nabla \boldsymbol{v}_0 \text{ for } z \to \pm l.
$$

Furthermore, a short calculation shows that

$$
\nabla_\Gamma \cdot (\sigma(C_0^\Gamma)\boldsymbol{I}) - \nabla_\Gamma \cdot (\sigma(C_0^\Gamma)\boldsymbol{\nu} \otimes \boldsymbol{\nu}) = \nabla_\Gamma \sigma(C_0^\Gamma) + \kappa\sigma(C_0^\Gamma)\boldsymbol{\nu}.
$$

So upon integrating from $-l$ to $+l$, matching, and using (4.1.8) we obtain

$$
[p_0]_1^2 \boldsymbol{\nu} - 2[\eta^{(i)} D(\boldsymbol{v_0})]_1^2 \boldsymbol{\nu} = \kappa\sigma(c_0^\Gamma)\boldsymbol{\nu} + \nabla_\Gamma \sigma(c_0^\Gamma). \tag{4.1.21}
$$

Inner equations and solutions to second order

Using $u_\Gamma = \boldsymbol{v}_0 \cdot \boldsymbol{\nu}$, $\partial_z C_0^\Gamma = \partial_z C_1^\Gamma = 0$, and equipartition of energy (4.1.12), equation (3.2.18) gives to order -1

$$\begin{aligned}
&\mathcal{W}\Big(\partial_t^\circ \left(2C_0^\Gamma W(\Phi_0)\right) + \boldsymbol{V}_0 \cdot \nabla_\Gamma \left(2C_0^\Gamma W(\Phi_0)\right) + (\boldsymbol{V}_1 \cdot \boldsymbol{\nu})\partial_z \left(2C_0^\Gamma W(\Phi_0)\right)\Big) \\
&= \mathcal{W}\partial_z\big(2M_\Gamma(C_0^\Gamma)W(\Phi_0)\gamma''(C_0^\Gamma)\partial_z C_2^\Gamma\big) + \mathcal{W}\nabla_\Gamma \cdot \big(2M_\Gamma(C_0^\Gamma)W(\Phi_0)\nabla_\Gamma\gamma'(C_0^\Gamma)\big) \\
&- 2W(\Phi_0)\sum_{i=1,2}\frac{\mathcal{W}}{\alpha^{(i)}}(\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)})).
\end{aligned}$$

Integrating from $-l$ to $+l$ and using (3.2.2), we obtain

$$\begin{aligned}
&\Big(\partial_t^\circ c_0^\Gamma + \boldsymbol{v}_0 \cdot \nabla_\Gamma c_0^\Gamma\Big) + \mathcal{W}\int_{-l}^{+l}(\boldsymbol{V}_1 \cdot \boldsymbol{\nu})\partial_z(2W(\Phi_0)C_0^\Gamma)dz \\
&= \mathcal{W}[2M_\Gamma(C_0^\Gamma)W(\Phi_0)\gamma''(C_0^\Gamma)\partial_z C_2^\Gamma]_{-l}^{+l} + \nabla_\Gamma \cdot \big(M_\Gamma(C_0^\Gamma)\nabla_\Gamma\gamma'(C_0^\Gamma)\big) \\
&- \sum_{i=1,2}\frac{1}{\alpha^{(i)}}(\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)})).
\end{aligned}$$

By (4.1.8), the jump term on the right hand side is zero. By (4.1.16) we have that

$$\begin{aligned}
&\int_{-l}^{+l}(\boldsymbol{V}_1 \cdot \boldsymbol{\nu})\partial_z(2C_0^\Gamma W(\Phi_0))dz \\
&= [2(\boldsymbol{V}_1 \cdot \boldsymbol{\nu})C_0^\Gamma W(\Phi_0)]_{-l}^{+l} - \int_{-l}^{+l} 2\partial_z(\boldsymbol{V}_1 \cdot \boldsymbol{\nu})W(\Phi_0)C_0^\Gamma dz \\
&= 0 + c_0^\Gamma \int_{-l}^{+l}(\nabla_\Gamma \cdot \boldsymbol{V}_0)2W(\Phi_0)dz = \mathcal{W}^{-1}c_0^\Gamma \nabla_\Gamma \cdot \boldsymbol{v}_0,
\end{aligned}$$

and by (4.1.19)

$$\sum_{i=1,2}\frac{1}{\alpha^{(i)}}(\gamma'(c_0^\Gamma) - G_i'(c_0^{(i)})) = [\boldsymbol{J}_{c,0}^{(i)}]_1^2\boldsymbol{\nu}.$$

Using $\partial_t^\bullet(\cdot) = \partial_t^\circ(\cdot) + \boldsymbol{v} \cdot \nabla_\Gamma(\cdot)$, we finally obtain the desired surface surfactant equation

$$\partial_t^\bullet c_0^\Gamma + c_0^\Gamma \nabla_\Gamma \cdot \boldsymbol{v}_0 - \nabla_\Gamma \cdot \big(M_\Gamma(c_0^\Gamma)\nabla_\Gamma\gamma'(c_0^\Gamma)\big) = [\boldsymbol{J}_{c,0}^{(i)}]_2^1\boldsymbol{\nu}. \tag{4.1.22}$$

Hence, from Model A we recover the equations of the sharp interface model for non-instantaneous adsorption.

4.1.4 Alternative asymptotic limit for Model A

Let us now assume that

$$\alpha^{(i)} = \varepsilon.$$

Then we obtain instantaneous adsorption (2.4.1) instead of (2.3.8) in the limit $\varepsilon \to 0$, which will be demonstrated in what follows.

Inner equations and solutions to leading and first order

We recover $[\boldsymbol{v}_0 \cdot \boldsymbol{\nu}]_1^2 = 0$ and obtain $\partial_z V_1 \cdot \boldsymbol{\nu} + \nabla_\Gamma \cdot \boldsymbol{V}_0 = 0$ from equation (3.2.13) to order -1 and to zeroth order respectively. From equation (3.2.15) we obtain $\partial_z M_0 = 0$ and $u_\Gamma = \boldsymbol{v}_0 \cdot \boldsymbol{\nu}$ to order -2 and to order -1 respectively. To order -2 equation (3.2.14) gives $[\boldsymbol{v}_0]_1^2 = 0$.

To order -3, the interfacial surfactant equation (3.2.18) gives $\partial_z C_0^\Gamma = 0$. This leads to the profile for Φ_0 and equipartition of energy (4.1.12) from (3.2.16). Furthermore, we obtain the solvability condition (4.1.20) from (3.2.16) at zeroth order and the jump in the stress tensor (4.1.21) from (3.2.14) at order -1.

To order -2 we obtain from (3.2.17) and (3.2.18)

$$-\partial_z\big(M_c^{(i)}(C_0^{(i)})\xi_i(\Phi_0)\partial_z G_i'(C_0^{(i)})\big) = 2\mathcal{W}W(\Phi_0)(\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)})), \tag{4.1.23}$$

$$\partial_z\big(M_\Gamma(C_0^\Gamma)W(\Phi_0)\partial_z(\gamma''(C_0^\Gamma)C_1^\Gamma)\big) = \sum_{i=1,2} W(\Phi_0)(\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)})). \tag{4.1.24}$$

Now, multiplying (4.1.23) by $G_i'(C_0^{(i)})$, $i = 1, 2$, and (4.1.24) by $2\mathcal{W}\gamma'(C_0^\Gamma)$ and subtracting gives

$$\begin{aligned}
&-\sum_{i=1,2} \partial_z\big(M_c^{(i)}\xi_i(\Phi_0)\partial_z G_i'(C_0^{(i)})\big)G_i'(C_0^{(i)}) + 2\mathcal{W}W(\Phi_0)\sum_{i=1,2}\left|\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)})\right|^2 \\
&- \partial_z\big(M_\Gamma 2\mathcal{W}W(\Phi_0)\partial_z(\gamma''(C_0^\Gamma)C_1^\Gamma)\big)\gamma'(C_0^\Gamma) = 0.
\end{aligned}$$

Integrating from $-l$ to $+l$, integrating by parts, and using $\partial_z C_0^\Gamma = 0$ yields

$$\begin{aligned}
0 = &\sum_{i=1,2}\int_{-l}^{+l} M_c^{(i)}\xi_i(\Phi_0)\left|\partial_z G_i'(C_0^{(i)})\right|^2 + 2\mathcal{W}W(\Phi_0)\left|\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)})\right|^2 dz \\
&- \big[M_\Gamma 2\mathcal{W}W(\Phi_0)\gamma''(C_0^\Gamma)\partial_z C_1^\Gamma\gamma'(C_0^\Gamma)\big]_{-l}^{+l} - \sum_{i=1,2}\big[M_c^{(i)}\xi_i(\Phi_0)\partial_z G_i'(C_0^{(i)})G_i'(C_0^{(i)})\big]_{-l}^{+l}.
\end{aligned}$$

The first jump term vanishes by (4.1.8), and when applying (4.1.5) to $C_0^{(i)}$ then the

second jump term is also zero, by (4.1.9). Hence we have

$$\sum_{i=1,2}\int_{-l}^{+l} M_c^{(i)}\xi_i(\Phi_0)\left|\partial_z G_i'(C_0^{(i)})\right|^2 + 2\mathcal{W}W(\Phi_0)\left|\gamma'(C_0^\Gamma) - G_i'(C_0^{(i)})\right|^2 dz = 0.$$

As all the terms are non-negative, this implies that

$$\partial_z C_0^{(i)} = 0 \quad \text{and} \quad \gamma'(C_0^\Gamma) = G_i'(C_0^{(i)}).$$

Inner equations and solutions to second order

Adding the surfactant equations (3.2.17) and (3.2.18), the order -1 terms yield

$$\begin{aligned}
&2\mathcal{W}W(\Phi_0)\big(\partial_t^\circ C_0^\Gamma + \boldsymbol{V}_0\cdot\nabla_\Gamma C_0^\Gamma\big) + \boldsymbol{V}_1\cdot\boldsymbol{\nu}\partial_z(2\mathcal{W}W(\Phi_0)C_0^\Gamma)\\
&= \partial_z\big(M_\Gamma 2\mathcal{W}W(\Phi_0)\gamma''(C_0^\Gamma)\partial_z C_2^\Gamma + M_\Gamma\mathcal{W}(\partial_z\Phi_0\partial_z\Phi_1 + W'(\Phi_0)\Phi_1)\gamma''(C_0^\Gamma)\partial_z C_1^\Gamma\big)\\
&+ \nabla_\Gamma\cdot(M_\Gamma 2\mathcal{W}W(\Phi_0)\nabla_\Gamma\gamma'(C_0^\Gamma)) + \sum_{i=1,2}\partial_z(M_c^{(i)}\xi_i(\Phi_0)G_i''(C_0^{(i)})\partial_z C_1^{(i)}).
\end{aligned}$$

Integrating from $-l$ to $+l$ and matching (4.1.6) applied to $\partial_z C_1^{(i)}$ or the matching condition (4.1.9) leads to (4.1.22) again. Hence, from Model A with the scaling $\alpha^{(i)} = \varepsilon$, we recover the equations of the sharp interface model with two-sided instantaneous adsorption.

4.1.5 Asymptotic analysis for Model B

Due to the equilibrium condition (3.3.1), we believe it is more appropriate to consider the flux in (3.3.12) as one term, rather than the sum of two separate fluxes. Hence, we express the surfactant equations in Model B as

$$\begin{aligned}
\partial_t^\bullet(\xi_1(\varphi)c^{(1)}) - \nabla\cdot(M_c^{(1)}(c^{(1)})\xi_1(\varphi)\nabla G_1'(c^{(1)})) \qquad (4.1.25)\\
= \frac{1}{\alpha^{(1)}}\delta(\varphi,\nabla\varphi)(G_2'(c^{(2)}) - G_1'(c^{(1)})),\\
\partial_t^\bullet(\xi_2(\varphi)c^{(2)} + \delta(\varphi,\nabla\varphi)g(c^{(2)})) + \nabla\cdot\boldsymbol{J}^* \qquad (4.1.26)\\
= -\frac{1}{\alpha^{(1)}}\delta(\varphi,\nabla\varphi)(G_2'(c^{(2)}) - G_1'(c^{(1)})),
\end{aligned}$$

where

$$\boldsymbol{J}^* := -\Big(M_c^{(2)}(c^{(2)})\xi_2(\varphi) + M_\Gamma(g(c^{(2)})\delta(\varphi,\nabla\varphi)\Big)\nabla G_2'(c^{(2)}).$$

Following Cahn, Elliott, and Novick-Cohen [1996], we assume that $\boldsymbol{J}^*$ has the following outer and inner expansions based on the outer and inner expansions of $\delta(\varphi, \nabla\varphi)$:

$$\boldsymbol{J}^* = \varepsilon^{-2}\boldsymbol{J}^{*,\text{bulk}}_{-2} + \varepsilon^{-1}\boldsymbol{J}^{*,\text{bulk}}_{-1} + \boldsymbol{J}^{*,\text{bulk}}_{0} + \dots,$$
$$\boldsymbol{J}^* = \varepsilon^{-2}\boldsymbol{J}^{*,\text{int}}_{-2} + \varepsilon^{-1}\boldsymbol{J}^{*,\text{int}}_{-1} + \boldsymbol{J}^{*,\text{int}}_{0} + \dots,$$

where, for example,

$$\begin{aligned}
\boldsymbol{J}^{*,\text{bulk}}_{-2} &= 0, \quad \boldsymbol{J}^{*,\text{bulk}}_{-1} = -\mathcal{W}M_\Gamma(g(c_0^{(2)}))W(\varphi_0)\nabla G_2'(c_0^{(2)}),\\
\boldsymbol{J}^{*,\text{bulk}}_{0} &= -\mathcal{W}(M_\Gamma'(g(c_0^{(2)}))c_1^{(2)}W(\varphi_0) + M_\Gamma(g(c_0^{(2)}))W'(\varphi_0)\varphi_1)\nabla G_2'(c_0^{(2)})\\
&\quad - \mathcal{W}M_\Gamma(g(c_0^{(2)}))W(\varphi_0)\nabla(G_2''(c_0^{(2)})c_1^{(2)}) - M_c^{(2)}(c_0^{(2)})\xi_2(\varphi_0)\nabla G_2'(c_0^{(2)}),\\
\boldsymbol{J}^{*,\text{int}}_{-2} &= -\mathcal{W}M_\Gamma(g(C_0^{(2)}))(\tfrac{1}{2}\,|\partial_z\Phi_0|^2 + W(\Phi_0))\partial_z G_2'(C_0^{(2)})\boldsymbol{\nu}.
\end{aligned}$$

The matching conditions for $\boldsymbol{J}^*$ are as follows (see Garcke and Stinner [2006]): As $z \to \pm l$,

$$\boldsymbol{J}^{*,\text{int}}_{-2}(t,s,z) \sim 0, \quad \partial_z\boldsymbol{J}^{*,\text{int}}_{-2}(t,s,z) \sim 0, \tag{4.1.27}$$
$$\boldsymbol{J}^{*,\text{int}}_{-1}(t,s,z) \sim (\boldsymbol{J}^{*,\text{bulk}}_{-1})^{\pm}(t,\boldsymbol{x})\cdot\boldsymbol{\nu}, \quad \partial_z\boldsymbol{J}^{*,\text{int}}_{-1}(t,s,z) \sim 0, \tag{4.1.28}$$
$$\boldsymbol{J}^{*,\text{int}}_{0}(t,s,z) \sim (\boldsymbol{J}^{*,\text{bulk}}_{0})^{\pm}(t,\boldsymbol{x}) + \nabla(\boldsymbol{J}^{*,\text{bulk}}_{-1})^{\pm}(t,\boldsymbol{x})\cdot\boldsymbol{\nu}z. \tag{4.1.29}$$

Outer equations and solutions

From equation (3.3.9) we obtain to order -1

$$0 = \mathcal{W}\sigma(g(c_0^{(2)}))W'(\varphi_0),$$

from which we obtain $\varphi_0 = \pm 1$, and regions $\Omega^{(1)}, \Omega^{(2)}$ defined as in the previous analysis. We also recover the usual fluid equation, incompressibility condition to zeroth order from (3.3.7) and (3.3.6).

From equation (4.1.26), to order -1, we have

$$\boldsymbol{J}^{*,\text{bulk}}_{-1} = -M_\Gamma(g(c_0^{(2)}))\mathcal{W}W(\varphi_0)\nabla G_2'(c_0^{(2)}) = 0. \tag{4.1.30}$$

To zeroth order we recover the bulk surfactant equation for $c^{(2)}$ from (4.1.26):

$$\partial_t^\bullet(\xi_2(\varphi_0)c_0^{(2)}) - \nabla\cdot(M_c^{(2)}\xi_2(\varphi_0)\nabla G_2'(c_0^{(2)})) = 0,$$

where $\xi_2(\varphi_0) = 0$ in $\Omega^{(1)}$ and $\xi_2(\varphi_0) = 1$ in $\Omega^{(2)}$. Similarly, we recover the bulk surfactant equation for $c^{(1)}$ from the zeroth order of (4.1.25).

Inner equations and solutions to leading and first order

We recover $[\boldsymbol{v}_0 \cdot \boldsymbol{\nu}]_-^+ = 0$ and obtain $\partial_z V_1 \cdot \boldsymbol{\nu} + \nabla_\Gamma \cdot \boldsymbol{V}_0 = 0$ from equation (3.3.6) to order -1 and to zeroth order respectively. From equation (3.3.8) we obtain $\partial_z M_0 = 0$ and $u_\Gamma = \boldsymbol{v}_0 \cdot \boldsymbol{\nu}$ to order -2 and to order -1 respectively. To order -2 equation (3.3.7) gives $[\boldsymbol{v}_0]_-^+ = 0$.

To order -3, we have from (4.1.26)

$$\partial_z \boldsymbol{J}_{-2}^{*,\text{int}} \cdot \boldsymbol{\nu} = 0, \text{ where } \boldsymbol{J}_{-2}^{*,\text{int}} = -\mathcal{W} M_\Gamma(\tfrac{1}{2}\,|\partial_z \Phi_0|^2 + W(\Phi_0))\partial_z G_2'(C_0^{(2)})\boldsymbol{\nu}.$$

This implies that $\boldsymbol{J}_{-2}^{*,\text{int}} \cdot \boldsymbol{\nu}$ is constant in z. Furthermore, for any $\boldsymbol{\tau}$ such that $\boldsymbol{\tau} \cdot \boldsymbol{\nu} = 0$, we have $\boldsymbol{J}_{-2}^{*,\text{int}} \cdot \boldsymbol{\tau} = 0$. Hence $\boldsymbol{J}_{-2}^{*,\text{int}} \equiv \boldsymbol{0}$ by (4.1.27) and this implies $\partial_z C_0^{(2)} = 0$ whenever $|\Phi_0| < 1$.

Equation (3.3.9) gives to order -1

$$0 = -\partial_z\big(\mathcal{W}\sigma(g(C_0^{(2)}))\partial_z \Phi_0\big) + \mathcal{W}\sigma(g(C_0^{(2)}))W'(\Phi_0).$$

Since $\partial_z C_0^{(2)} = 0$, we obtain $0 = -\partial_{zz}\Phi_0 + W'(\Phi_0)$ again, which gives the profile for Φ_0 and the equipartition of energy (4.1.12). Hence, we obtain the same solvability condition for Φ_1 from equation (3.3.9):

$$2\mu_0 = \sigma(g(c_0^{(2)}))\kappa + [G_i(c_0^{(i)}) - G_i'(c_0^{(i)})c_0^{(i)}]_1^2.$$

As previously, equation (3.3.7) then gives to order -1

$$[p_0]_1^2 \boldsymbol{\nu} - 2[\eta^{(i)} D(\boldsymbol{v}_0)]_1^2 \boldsymbol{\nu} = \kappa\sigma(g(c_0^{(2)}))\boldsymbol{\nu} + \nabla_\Gamma \sigma(g(c_0^{(2)})).$$

Meanwhile, equation (4.1.25) gives to order -2

$$\partial_z(M_c^{(1)}(C_0^{(1)})\xi_1(\Phi_0)\partial_z G_1'(C_0^{(1)})) = 0,$$

and so $\partial_z C_0^{(1)} = 0$. To order -1, we obtain

$$-\frac{2}{\alpha^{(1)}}\mathcal{W}W(\Phi_0)(G_2'(C_0^{(2)}) - G_1'(C_0^{(1)})) = \partial_z(M_c^{(1)}(C_0^{(1)})\xi_1(\Phi_0)\partial_z(G_1''(C_0^{(1)})C_1^{(1)})).$$

Integrating from $-l$ to $+l$, using matching (4.1.6) and the property that $\xi_1(+1) = 0, \xi_1(-1) = 1$ lead to

$$M_c^{(1)}(c_0^{(1)})\nabla G_1'(c_0^{(1)}) = \frac{1}{\alpha^{(1)}}(G_2'(c_0^{(2)}) - G_1'(c_0^{(1)})). \tag{4.1.31}$$

To order -2, equation (4.1.26) gives

$$\partial_z \boldsymbol{J}_{-1}^{*,\mathrm{int}} \cdot \boldsymbol{\nu} = \partial_z (\boldsymbol{J}_{-1}^{*,\mathrm{int}} \cdot \boldsymbol{\nu}) = 0,$$

where, thanks to $\partial_z C_0^{(2)} = 0$,

$$\boldsymbol{J}_{-1}^{*,\mathrm{int}} = -M_\Gamma(g(C_0^{(2)}))2\mathcal{W}W(\Phi_0)(\nabla_\Gamma G_2'(C_0^{(2)}) + \partial_z(G_2''(C_0^{(2)})C_1^{(2)})\boldsymbol{\nu}).$$

This implies that

$$\partial_z\big(M_\Gamma(g(C_0^{(2)}))2\mathcal{W}W(\Phi_0)\partial_z(G_2''(C_0^{(2)})C_1^{(2)})\big) = 0.$$

Integrating from $-l$ to z and using (4.1.8) yields

$$\partial_z C_1^{(2)} = 0 \text{ whenever } |\Phi_0| < 1.$$

Inner equations and solutions to second order

To order -1, equation (4.1.26) gives

$$\begin{aligned} &2\mathcal{W}W(\Phi_0)\big(\partial_t^\circ g(C_0^{(2)}) + \boldsymbol{V}_0 \cdot \nabla_\Gamma g(C_0^{(2)})\big) + \boldsymbol{V}_1 \cdot \boldsymbol{\nu}\partial_z(2\mathcal{W}W(\Phi_0)g(C_0^{(2)})) \\ &\qquad = -\nabla_\Gamma \cdot \boldsymbol{J}_{-1}^{\mathrm{int}} - \partial_z \boldsymbol{J}_0^{\mathrm{int}} \cdot \boldsymbol{\nu} - \frac{1}{\alpha^{(1)}} 2\mathcal{W}W(\Phi_0)(G_2'(C_0^{(2)}) - G_1'(C_0^{(1)})), \end{aligned}$$

where, using the already obtained results, $\boldsymbol{J}_{-1}^{\mathrm{int}} = -M_\Gamma(g(c_0^{(2)}))2\mathcal{W}W(\Phi_0)\nabla_\Gamma G_2'(C_0^{(2)})$.

Proceeding as above, the left hand side yields

$$\partial_t^\bullet g(c_0^{(2)}) + g(c_0^{(2)})\nabla_\Gamma \cdot \boldsymbol{v}_0.$$

For the right hand side, the integration from $-l$ to $+l$ gives

$$-\nabla_\Gamma \cdot \left(\int_{-l}^{+l} \boldsymbol{J}_{-1}^{\mathrm{int}}\right) - \boldsymbol{J}_0^{\mathrm{int}} \cdot \boldsymbol{\nu}\big|_{-l}^{+l} - \frac{1}{\alpha^{(1)}}(G_2'(c_0^{(2)}) - G_1'(c_0^{(1)})),$$

where

$$-\nabla_\Gamma \cdot \left(\int_{-l}^{+l} \boldsymbol{J}_{-1}^{\mathrm{int}}\right) = \nabla_\Gamma \cdot \big(M_\Gamma(g(c_0^{(2)}))\nabla_\Gamma G_2'(c_0^{(2)})\big),$$

and (4.1.29), (4.1.30) and (4.1.31) give

$$
\begin{aligned}
&- \boldsymbol{J}_0^{\text{int}} \cdot \boldsymbol{\nu}\big|_{-l}^{+l} - \frac{1}{\alpha^{(1)}}(G_2'(c_0^{(2)}) - G_1'(c_0^{(1)})) = - \boldsymbol{J}_0^{\text{bulk}} \cdot \boldsymbol{\nu}\Big|_{-}^{+} - \frac{1}{\alpha^{(1)}}(G_2'(c_0^{(2)}) - G_1'(c_0^{(1)})) \\
&= \big(M_c^{(2)} \nabla G_2'(c_0^{(2)}) - M_c^{(1)} \nabla G_1'(c_0^{(1)})\big) \cdot \boldsymbol{\nu} = [\boldsymbol{J}_{c,0}^{(i)}]_2^1 \boldsymbol{\nu}.
\end{aligned}
$$

So, we obtain the surface surfactant equation

$$
\partial_t^\bullet g(c_0^{(2)})) + g(c_0^{(2)}) \nabla_\Gamma \cdot \boldsymbol{v}_0 = \nabla_\Gamma \cdot \big(M_\Gamma \nabla_\Gamma G_2'(c_0^{(2)})\big) + [\boldsymbol{J}_{c,0}^{(i)}]_2^1 \boldsymbol{\nu}.
$$

Hence, from Model B, we recover the equations of the sharp interface model with one-sided instantaneous adsorption and one-sided non-instantaneous adsorption.

4.1.6 Asymptotic analysis for Model C

The asymptotic analysis for Model C is similar to that for Model B, and so we will only sketch the analysis for Model C.

We express (3.4.8) as

$$
\partial_t^\bullet (\xi_1(\varphi) c^{(1)}(q) + \xi_2(\varphi) c^{(2)}(q) + \delta(\varphi, \nabla\varphi) c^\Gamma(q)) + \nabla \cdot \boldsymbol{J} = 0, \tag{4.1.32}
$$

where

$$
\boldsymbol{J} := -\big(M_c^{(1)} \xi_1(\varphi) + M_c^{(2)} \xi_2(\varphi) + M_\Gamma \delta(\varphi, \nabla\varphi)\big) \nabla q.
$$

Based on the outer and inner expansions of $\delta(\varphi, \nabla\varphi)$, we assume that $\boldsymbol{J}$ has the following outer and inner expansions:

$$
\begin{aligned}
\boldsymbol{J} &= \varepsilon^{-2} \boldsymbol{J}_{-2}^{\text{bulk}} + \varepsilon^{-1} \boldsymbol{J}_{-1}^{\text{bulk}} + \boldsymbol{J}_0^{\text{bulk}} + \dots, \\
\boldsymbol{J} &= \varepsilon^{-2} \boldsymbol{J}_{-2}^{\text{int}} + \varepsilon^{-1} \boldsymbol{J}_{-1}^{\text{int}} + \boldsymbol{J}_0^{\text{int}} + \dots,
\end{aligned}
$$

where, for example,

$$
\begin{aligned}
\boldsymbol{J}_{-2}^{\text{bulk}} &= 0, \quad \boldsymbol{J}_{-1}^{\text{bulk}} = -\mathcal{W} M_\Gamma(c_0^\Gamma) W(\varphi_0) \nabla q_0, \\
\boldsymbol{J}_0^{\text{bulk}} &= -\mathcal{W}(M_\Gamma(c^\Gamma(q_0)) W'(\varphi_0)\varphi_1 + M_\Gamma'(c^\Gamma(q_0)) q_1) \nabla q_0 \\
&\quad - \mathcal{W} M_\Gamma(c^\Gamma(q_0)) W(\varphi_0) \nabla q_1 - \sum_{i=1,2} M_c^{(i)}(c^{(i)}(q_0)) \xi_i(\varphi_0) \nabla q_0, \\
\boldsymbol{J}_{-2}^{\text{int}} &= -\mathcal{W} M_\Gamma(C_0^\Gamma)(\tfrac{1}{2} |\partial_z \Phi_0|^2 + W(\Phi_0)) \partial_z Q_0 \boldsymbol{\nu},
\end{aligned}
$$

and the matching conditions for $\boldsymbol{J}$ are the same as for $\boldsymbol{J}^*$ in Section 4.1.5.

Outer equations and solutions

From equation (3.4.7) we obtain to order -1

$$0 = \mathcal{W}\tilde{\sigma}(q_0)W'(\varphi_0),$$

from which we obtain $\varphi_0 = \pm 1$, and regions $\Omega^{(1)}, \Omega^{(2)}$ defined as in the previous analysis. We also recover the usual fluid equation, incompressibility condition to zeroth order.

With respect to the surfactant, to order -1 we have

$$\boldsymbol{J}_{-1}^{\text{bulk}} = -M_\Gamma \mathcal{W} W(\varphi_0)\nabla q_0 = 0. \tag{4.1.33}$$

To zeroth order we recover the bulk surfactant equations from (4.1.32):

$$\partial_t^\bullet(\xi_1(\varphi_0)c^{(1)}(q_0) + \xi_2(\varphi_0)c^{(2)}(q_0)) - \nabla\cdot(M_c^{(1)}\xi_1(\varphi_0)\nabla q_0 + M_c^{(2)}\xi_2(\varphi_0)\nabla q_0) = 0,$$

where we use $\xi_1(\varphi_0) = \xi_1(1) = 0$ in $\Omega^{(2)}$ and $\xi_2(\varphi_0) = \xi_2(-1) = 0$ in $\Omega^{(1)}$.

Inner equations and solutions to leading and first order

We recover $[\boldsymbol{v}_0\cdot\boldsymbol{\nu}]_-^+ = 0$ and obtain $\partial_z V_1\cdot\boldsymbol{\nu} + \nabla_\Gamma\cdot\boldsymbol{V}_0 = 0$ from equation (3.4.4) to orders -1 and to zeroth order respectively. From equation (3.4.6) we obtain $\partial_z M_0 = 0$ and $u_\Gamma = \boldsymbol{v}_0\cdot\boldsymbol{\nu}$ to order -2 and to order -1 respectively. To order -2 equation (3.4.5) gives $[\boldsymbol{v}_0]_-^+ = 0$.

To order -3, we have from (4.1.32)

$$\partial_z \boldsymbol{J}_{-2}^{\text{int}}\cdot\boldsymbol{\nu} = -\partial_z(\mathcal{W}M_\Gamma(\tfrac{1}{2}|\partial_z\Phi_0|^2 + W(\Phi_0))\partial_z Q_0) = 0,$$

The same analysis for Model B then implies that $\boldsymbol{J}_{-2}^{\text{int}} \equiv \boldsymbol{0}$ and $\partial_z Q_0 = 0$ whenever $|\Phi_0| < 1$.

To order -1, equation (3.4.7) gives the same profile for Φ_0 and the equipartition of energy (4.1.12). Furthermore, to zeroth order, we obtain the same solvability condition for Φ_1:

$$2\mu_0 = \tilde{\sigma}(q_0)\kappa + [G_i(c^{(i)}(q_0)) - q_0 c^{(i)}(q_0)]_1^2.$$

To order -1, equation (3.3.7) gives

$$[p_0]_1^2\boldsymbol{\nu} - 2[\eta^{(i)}D(\boldsymbol{v}_0)]_1^2\boldsymbol{\nu} = \kappa\tilde{\sigma}(q_0)\boldsymbol{\nu} + \nabla_\Gamma\tilde{\sigma}(q_0).$$

As $\partial_z Q_0 = 0$, to order -2, we have from (4.1.32)

$$\partial_z \boldsymbol{J}_{-1}^{\text{int}} \cdot \boldsymbol{\nu} = -\partial_z (M_\Gamma(c^\Gamma(Q_0)) 2\mathcal{W}W(\Phi_0)\partial_z Q_1) = 0.$$

Upon integrating from $-l$ to z and using (4.1.8) yields

$$\partial_z Q_1 = 0 \text{ whenever } |\Phi_0| < 1.$$

Inner equations and solutions to second order

To order -1, equation (4.1.32) gives

$$\begin{aligned} 2\mathcal{W}W(\Phi_0)\big(\partial_t^\circ c^\Gamma(Q_0) + \boldsymbol{V}_0 \cdot \nabla_\Gamma c^\Gamma(Q_0)\big) + \boldsymbol{V}_1 \cdot \boldsymbol{\nu}\partial_z(2\mathcal{W}W(\Phi_0)c^\Gamma(Q_0)) \\ = \nabla_\Gamma \cdot (M_\Gamma(c^\Gamma(Q_0))2\mathcal{W}W(\Phi_0)\nabla_\Gamma Q_0) - \partial_z \boldsymbol{J}_0^{\text{int}} \cdot \boldsymbol{\nu}. \end{aligned}$$

Proceeding as above, the left hand side yields

$$\partial_t^\bullet(c^\Gamma(q_0)) + c^\Gamma(q_0)\nabla_\Gamma \cdot \boldsymbol{v}_0.$$

For the right hand side, the integration from $-l$ to $+l$ and (4.1.29), (4.1.33) give

$$-\boldsymbol{J}_0^{\text{int}} \cdot \boldsymbol{\nu}\big|_{-l}^{+l} = -\boldsymbol{J}_0^{\text{bulk}} \cdot \boldsymbol{\nu}\Big|_{-}^{+} = -\big(-M_c^{(2)}\nabla q_0 + M_c^{(1)}\nabla q_0\big) \cdot \boldsymbol{\nu} = [\boldsymbol{J}_{c,0}^{(i)}]_2^1 \boldsymbol{\nu}.$$

Hence we obtain

$$\partial_t^\bullet(c^\Gamma(q_0)) + c^\Gamma(q_0)\nabla_\Gamma \cdot \boldsymbol{v}_0 = \nabla_\Gamma \cdot \big(M_\Gamma \nabla_\Gamma q_0\big) + [\boldsymbol{J}_{c,0}^{(i)}]_2^1 \boldsymbol{\nu},$$

and conclude that, from Model C, we recover the equations of the sharp interface model with two-sided instantaneous adsorption.

4.2 Numerical experiments

In this section we report on numerical experiments that serve to support the above asymptotic analysis and illustrate that the proposed phase field models are able to describe phenomena that can be observed in physical experiments. Since the phase field approach to two-phase flow has been intensively studied already and the extension consists of accounting for the surfactant dynamics, the numerical experiments are designed to focus on the latter one.

4.2.1 Surfactant adsorption dynamics in 1D

We first carefully investigate the adsorption of surfactants to interfaces in a one-dimensional setting where we exclude the effects of fluid transport ($\boldsymbol{v} = \boldsymbol{0}$) and focus on the dynamics between bulk and interfacial surfactants. We assume that the surfactant is insoluble in $\Omega^{(1)}$ and the sharp interface model is a variant of the Ward–Tordai problem defined on a bounded domain. For the phase field models we assume that φ is given, and so the dimensionless surfactant equations (3.5.11) and (3.5.12) of Model A simplify down to (dropping the index $*$ and the index 2 for the bulk phase)

$$\begin{aligned}\partial_t\big(\xi(\varphi)c\big) - \partial_x\Big(\frac{1}{\mathrm{Pe}_c}\xi(\varphi)\partial_x c\Big) &= \frac{1}{\alpha}\delta(\varphi,\partial_x\varphi)\big(\gamma'(c^\Gamma) - G'(c)\big),\\ \partial_t\big(\delta(\varphi,\partial_x\varphi)c^\Gamma\big) - \partial_x\Big(\frac{1}{\mathrm{Pe}_\Gamma}\delta(\varphi,\partial_x\varphi)\partial_x c^\Gamma\Big) &= -\frac{1}{\alpha}\delta(\varphi,\partial_x\varphi)\big(\gamma'(c^\Gamma) - G'(c)\big).\end{aligned}$$

For Model B we have one equation from (3.5.14) instead,

$$\partial_t\big(\xi(\varphi)c + \delta(\varphi,\partial_x\varphi)g(c)\big) - \partial_x\Big(\frac{1}{\mathrm{Pe}_c}\xi(\varphi)\partial_x c + \frac{1}{\mathrm{Pe}_\Gamma}\delta(\varphi,\partial_x\varphi)\partial_x c\Big) = 0,$$

and for Model C, we replace $c, g(c), \partial_x c$ by $c(q), c^\Gamma(q), \partial_x q$ in the above equation.

We remark that the equations for Model C in this setting is structurally similar to the equation of Model B. Hence in the subsequent one-dimensional experiments we will only compare Models A and B, while Model C will be the subject of investigation in the two-dimensional experiments due to its two-sided nature.

To support the asymptotic analysis we test

- the ε-convergence of the profile of $c(x,1)$;
- the ε-convergence of the profile of $c^\Gamma(0,t)$;
- the ε-convergence of $\big|\gamma'(c^\Gamma) - G'(c)\big|$ at $x = 0, t = 1$.

The third test only applies to Model A when α is scaled with ε, as the Dirichlet-type condition $\gamma'(c^\Gamma) = G'(c)$ for instantaneous adsorption is enforced in the limit $\varepsilon \to 0$.

To measure the ε-convergence of the profiles, we look at the difference $|c_{PF} - c_{SI}|$ and $\big|c^\Gamma_{PF} - c^\Gamma_{SI}\big|$, where $c^\Gamma_{PF}(x,t)$ and $c_{PF}(x,t)$ are the interfacial and bulk densities of the phase field models respectively, while $c^\Gamma_{SI}(t)$ and $c_{SI}(x,t)$ denote the interfacial and bulk densities of the sharp interface model respectively. We will be comparing $\{(4.2.1),(4.2.2)\}$ with Model A ($\alpha > 0$) and $\{(4.2.1),(4.2.3)\}$ with Model A ($\alpha = \varepsilon$) and Model B. The numerical methods described in this section have been

implemented using the software MATLAB, Version 7.11.0 (R2010b), [MATLAB, 2010].

Sharp interface model

Set $\Omega = [0,1]$ and Γ as the origin, the dimensionless sharp interface model is

$$\begin{aligned} \partial_t c &= \frac{1}{\mathrm{Pe}_c}\partial_{xx} c, \quad \text{in } (0,1], \\ \partial_t c^\Gamma &= \frac{1}{\mathrm{Pe}_c}\partial_x c, \quad \text{at } x = 0, \end{aligned} \tag{4.2.1}$$

together with

$$\frac{\alpha}{\mathrm{Pe}_c}\partial_x c = -(\gamma'(c^\Gamma) - G'(c)), \text{ at } x = 0, \tag{4.2.2}$$

for non-instantaneous adsorption or

$$c^\Gamma(t) = g(t) = (\gamma')^{-1}(G'(c))), \text{ at } x = 0, \tag{4.2.3}$$

for instantaneous adsorption. We impose the following initial-boundary conditions:

$$c(x = 1, t) = 1, \quad c(x, t = 0) = 1, \quad c^\Gamma(t = 0) = c_0^\Gamma.$$

This is a version of the Ward–Tordai problem on a bounded interval. We solve the problem via a finite-difference scheme: Let $0 = x_1 < \cdots < x_N = 1$ be a uniform discretisation of Ω with mesh size $h = 1/N$. Let $\Delta t = 1/N_f$ for integer $N_f \in \mathbb{N}$ be a time step and define $t_n = n\Delta t$ for $n = 0, \ldots, N_f$. Let $\theta = \Delta t/(\mathrm{Pe}_c h^2)$ and denote $c^n(x) = c(x, t_n)$. Then given $\boldsymbol{c}^n = (c^n(x_1), \ldots, c^n(x_{N-1}), c^n(x_N))$, the solution at time t_n, we solved for $\boldsymbol{c}^{n+1} = (c^{n+1}(x_1), \ldots, c^{n+1}(x_{N-1}), c^{n+1}(x_N))$, which for $\{(4.2.1), (4.2.2)\}$ satisfies

$$\begin{pmatrix} 1+2\theta & -2\theta & \ldots & \ldots & 0 \\ -\theta & 1+2\theta & -\theta & \ldots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \ldots & -\theta & 1+2\theta & -\theta \\ 0 & \ldots & \ldots & 0 & 1 \end{pmatrix} \boldsymbol{c}^{n+1} = \begin{pmatrix} c^n(x_1) + 2h\theta D^n \\ c^n(x_2) \\ \vdots \\ c^n(x_{N-1}) \\ 1 \end{pmatrix},$$

where

$$D^n := \frac{\mathrm{Pe}_c}{\alpha}(\gamma'(c^{\Gamma,n}) - G'(c^n(x_1))),$$

and then we set

$$c^{\Gamma,n+1} = c^{\Gamma,n} + \theta h(c^{n+1}(x_2) - c^{n+1}(x_1)).$$

For $\{(4.2.1), (4.2.3)\}$, we have to solve

$$\begin{pmatrix} \theta h & -\theta h & 0 & \dots & \dots & 0 \\ -\theta & 1+2\theta & -\theta & 0 & \dots & 0 \\ \vdots & \ddots & \ddots & \ddots & \ddots & \vdots \\ 0 & \dots & 0 & -\theta & 1+2\theta & -\theta \\ 0 & \dots & \dots & \dots & 0 & 1 \end{pmatrix} \boldsymbol{c}^{n+1} + \begin{pmatrix} g(c^{n+1}(x_1)) \\ 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} g(c^n(x_1)) \\ c^n(x_2) \\ \vdots \\ c^n(x_{N-1}) \\ 1 \end{pmatrix}.$$

Phase field model

We use the one-sided version for each of the above phase field models. We choose the potential W to be of double-obstacle type and hence $\mathcal{W} = \frac{2}{\pi}$ (see (3.2.2)). This has the advantage that the phase field variable φ lies strictly in the interval $[-1, 1]$ and interfacial layer has constant width equal to $\varepsilon\pi$. The asymptotic analysis suggests that to leading order

$$\varphi(x) = \begin{cases} 1, & \text{if } x > \varepsilon\frac{\pi}{2}, \\ \sin(\frac{x}{\varepsilon}), & \text{if } |x| \leq \varepsilon\frac{\pi}{2}, \\ -1, & \text{if } x < -\varepsilon\frac{\pi}{2}, \end{cases}$$

and thanks to equipartition of energy $\delta(\varphi, \partial_x\varphi)$ simplifies to

$$\delta(\varphi, \partial_x\varphi) = \begin{cases} \frac{1}{\varepsilon}\left|\cos(\frac{x}{\varepsilon})\right|^2, & \text{if } |x| \leq \varepsilon\frac{\pi}{2}, \\ 0, & \text{if } |x| > \varepsilon\frac{\pi}{2}. \end{cases}$$

We choose $\xi(\varphi)$ to be

$$\xi(x) = \frac{1}{2}\left(1 + \frac{1}{2}\varphi(x)(3 - \varphi(x)^2)\right).$$

For the discretisation we employ linear finite elements. Let $\Delta t = \frac{1}{N_f}$ for integer $N_f \in \mathbb{N}$ be a time step and define $t_n = n\Delta t$ for $n = 0, \dots, N_f$. Let $\mathcal{T}_h$ be a uniform subdivision of the interval $[-1, 1]$ consisting of subintervals with size h. Let N be the number of vertices with coordinates denoted by $\{x_1, \cdots, x_N\}$. Let $\mathcal{N}$ be the set of vertex indices and for an index $i \in \mathcal{N}$ let ω_i denote the neighbouring vertices connected to vertex i (i.e. $w_i = \{x_{i-1}, x_{i+1}\}$). Furthermore, based on the

functional form of δ and ξ, we define

$$\mathcal{X}_h = \{i \in \mathcal{N} : \text{ there exists } j \in \omega_i \text{ such that } \xi(x_j) > 0\}, \tag{4.2.4}$$

$$\mathcal{D}_h = \{i \in \mathcal{N} : \text{ there exists } j \in \omega_i \text{ such that } \delta(x_j) > 0\}. \tag{4.2.5}$$

In the implementation, we define $y^{\pm}$ to be the vertices such that $y^+ - h < \varepsilon\frac{\pi}{2} < y^+$ and $y^- < -\varepsilon\frac{\pi}{2} < y^- + h$. Then, for any $i \in \mathcal{N}$, we set

$$\varphi(x_i) = \begin{cases} 1, & \text{if } x_i \geq y^+, \\ \sin\left(\frac{x_i}{\varepsilon}\right), & \text{if } y^- \leq x_i \leq y^+, \\ -1, & \text{if } x_i \leq y^-. \end{cases}$$

Consequently, $\mathcal{D}_h$ consists of all the vertices that lie between y^- and y^+, while $\mathcal{X}_h$ consists of all vertices that lie in between y^- and 1. Let

$$\mathcal{S}^h := \{v_h \in C^0([-1,1])\colon v_h \in P^1([x_i, x_{i+1}]), i = 1, \ldots, N-1\} \tag{4.2.6}$$

be the discrete finite-element space. For $\eta \in C^0([-1,1])$ we define the interpolation operator $\Pi^h : C^0([-1,1]) \to \mathcal{S}^h$ to be

$$\Pi^h(\eta) := \sum_{i=1}^{N} \eta(x_i)\chi_i, \tag{4.2.7}$$

where $\chi_j(x)$ denote the standard basis function such that $\chi_j \in C^0([-1,1])$ and χ_j is a linear polynomial on each interval $[x_i, x_{i+1}]$ satisfying $\chi_j(x_i) = \delta_{ji}$ for all $i, j = 1, \ldots, N$. Using the method of Elliott et al. [2011], we can find the finite-element function $c_h^{\Gamma,n+1}(x) = c_h^{\Gamma}(x, t_{n+1}) \in \mathcal{S}^h$ such that $c_h^{\Gamma,n+1}(x_j) = 0$ if $j \notin \mathcal{D}_h$ and satisfies

$$\begin{aligned} &\frac{1}{\Delta t}\left(\int_{-1}^{1} \Pi^h(\delta c_h^{\Gamma,n+1}\chi_j) - \Pi^h(\delta c_h^{\Gamma,n}\chi_j)\right) + \int_{-1}^{1} \frac{1}{\mathrm{Pe}_\Gamma}\Pi^h(\delta)\partial_x c_h^{\Gamma,n+1}\partial_x\chi_j \\ &\quad = -\int_{-1}^{1} \Pi^h(\alpha^{-1}\delta(\gamma'(c_h^{\Gamma,n}) - G'(c_h^n))\chi_j), \quad \forall j \in \mathcal{D}_h. \end{aligned}$$

The method for $c_h^{n+1}(x) = c_h(x, t_{n+1}) \in \mathcal{S}^h$ is analogous, whereby $c_h^{n+1}(x_j) = 0$ if

$j \notin \mathcal{X}_h$ and satisfies

$$\frac{1}{\Delta t}\left(\int_{-1}^{1}\Pi^h(\xi c_h^{n+1}\chi_j)-\Pi^h(\xi c_h^n\chi_j)\right)+\int_{-1}^{1}\frac{1}{\mathrm{Pe}_c}\Pi^h(\xi)\partial_x c_h^{n+1}\partial_x\chi_j$$
$$=\int_{-1}^{1}\Pi^h(\alpha^{-1}\delta(\gamma'(c_h^{\Gamma,n})-G'(c_h^n))\chi_j),\quad \forall j\in\mathcal{X}_h.$$

For Model B, we seek $c_h^{n+1}\in\mathcal{S}^h$ such that $c_h^{n+1}(x_j)=0$ if $j\notin\mathcal{X}_h\cup\mathcal{D}_h$ and satisfies

$$\frac{1}{\Delta t}\left(\int_{-1}^{1}\Pi^h((\xi c_h^{n+1}+\delta g(c_h^{n+1}))\chi_j)-\int_{-1}^{1}\Pi^h((\xi c_h^{n}+\delta g(c_h^{n}))\chi_j)\right)$$
$$+\int_{-1}^{1}\Pi^h\left(\frac{\xi}{\mathrm{Pe}_c}+\frac{\delta}{\mathrm{Pe}_\Gamma}\right)\partial_x c_h^{n+1}\partial_x\chi_j=0,\quad \forall j\in\mathcal{X}_h\cup\mathcal{D}_h.$$

Numerics for Model A

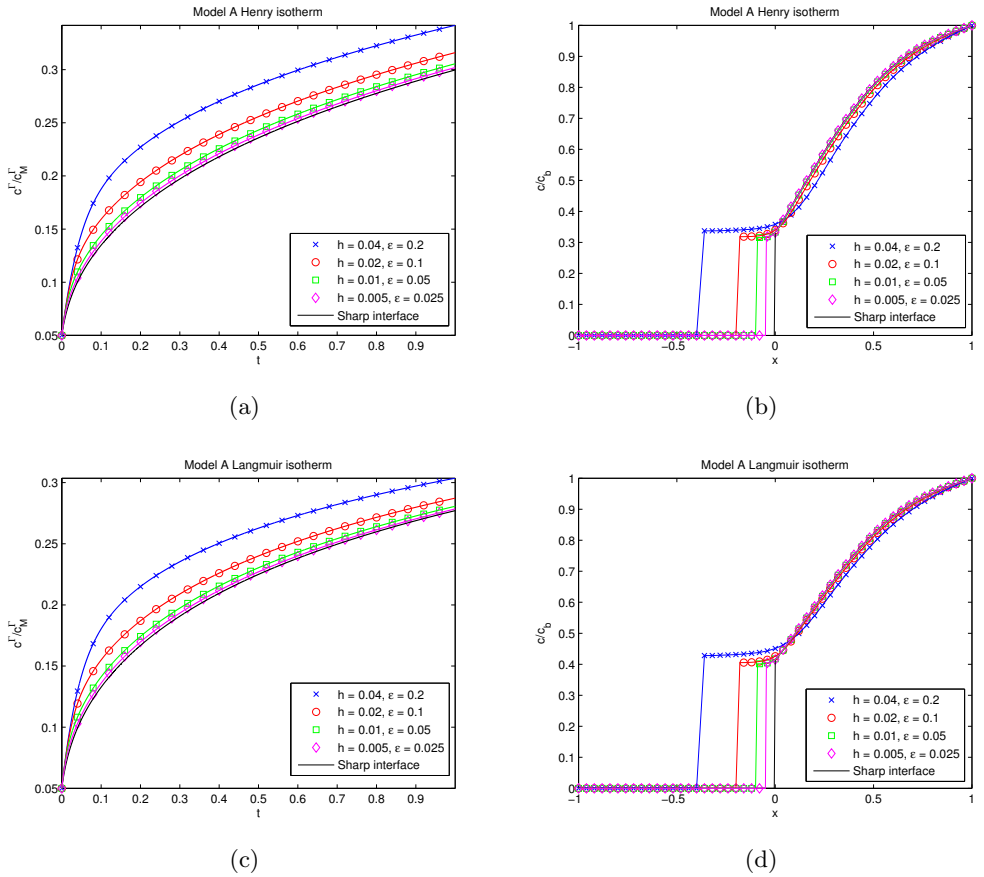
We choose $\alpha=1$, $\mathrm{Pe}_\Gamma=0.01$ and $\mathrm{Pe}_c=10$. The other parameters of the model are $c_M^\Gamma=1$, $c(x,0)=1$, $c^\Gamma(x,0)=0.05$, $B=1$, $K=1$. The mesh size h is taken from $\{0.08,0.04,0.02,0.01,0.005\}$ and the corresponding value of ε is chosen from $\{0.4,0.2,0.1,0.05,0.025\}$. To ensure that the numerical scheme is stable, for each test we choose a time step $\Delta t\le h^2$.

In the case of fixed $\alpha>0$ we refer to Table 4.1 for the ε-convergence in the difference in $c^\Gamma(0,1)$ and $c(0,1)$ between the phase field model and the sharp interface model and Figure 4.1 for the ε-convergence of the profiles.

h	ε	$\lvert c_{PF}^\Gamma(0,1)-c_{SI}^\Gamma(1)\rvert$	$\lvert c_{PF}(0,1)-c_{SI}(0,1)\rvert$
0.08	0.4	0.0974417	0.0732749
0.04	0.2	0.0419969	0.0265120
0.02	0.1	0.0163026	0.0076752
0.01	0.05	0.0058420	0.0015298
0.005	0.025	0.0022358	0.0002207
h	ε	$\lvert c_{PF}^\Gamma(0,1)-c_{SI}^\Gamma(1)\rvert$	$\lvert c_{PF}(0,1)-c_{SI}(0,1)\rvert$
0.08	0.4	0.0596860	0.0963854
0.04	0.2	0.0265857	0.0364079
0.02	0.1	0.0102234	0.0115916
0.01	0.05	0.0035830	0.0030918
0.005	0.025	0.0013697	0.0009629

Table 4.1: Convergence table for Model A, non-instantaneous adsorption ($\alpha=1$), Henry isotherm (top) and Langmuir isotherm (bottom).

We also considered the scaling $\alpha=\varepsilon$ and from Figure 4.2 and Tables 4.2 and 4.3 we observed the ε-convergence in the difference in $c^\Gamma(0,1)$ and $c(0,1)$ between



(a) (b)

(c) (d)

Figure 4.1: Model A ε-convergence for (a) the profile of $c^\Gamma(x=0,t)$ and (b) the profile of $c(x,t=1)$ with the Henry isotherm, (c) the profile of $c^\Gamma(x=0,t)$ and (d) the profile of $c(x,t=1)$ with the Langmuir isotherm. The parameter α is chosen to be 1.

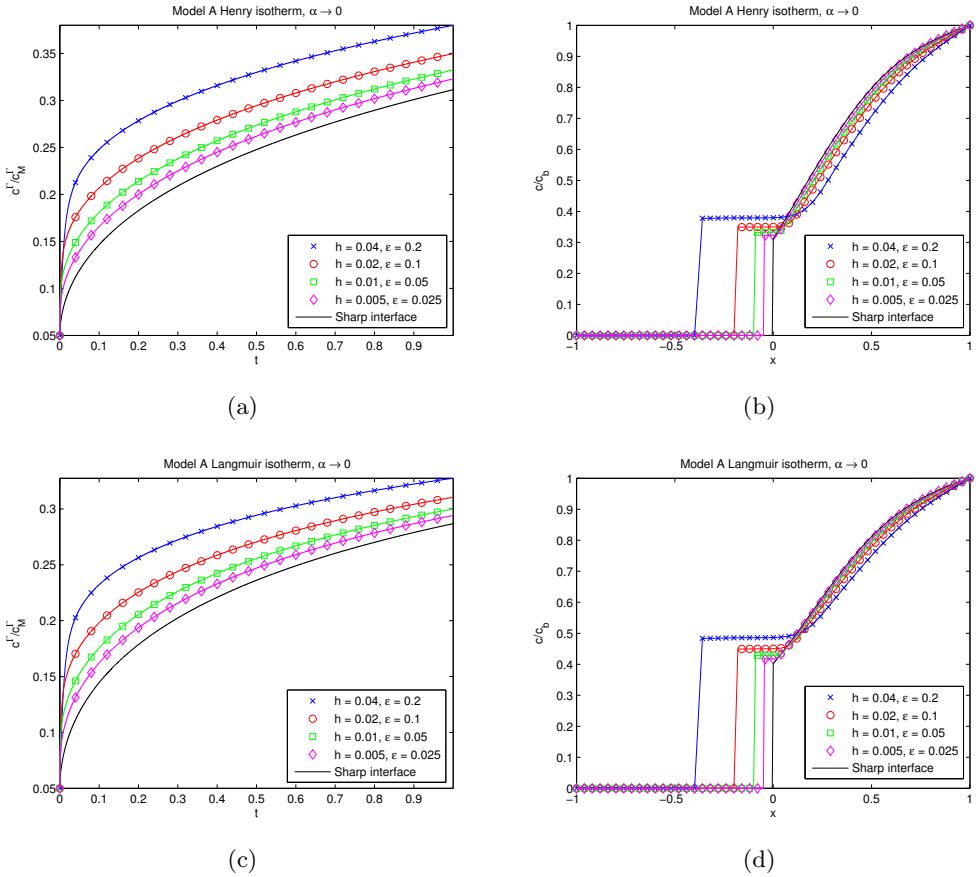


Figure 4.2: Model A, ε-convergence for (a) the profile of $c^\Gamma(x=0,t)$ and (b) the profile of $c(x,t=1)$ with the Henry isotherm, (c) the profile of $c^\Gamma(x=0,t)$ and (d) the profile of $c(x,t=1)$ with the Langmuir isotherm. The parameter α is chosen to be ε.

the phase field model and the sharp interface model. Furthermore, we note that the maximum and mean difference of $\left|\gamma'(c^\Gamma) - G'(c)\right|$ in the interfacial layer decreases linearly as $\varepsilon \to 0$.

h	ε	$\left\|c^\Gamma_{PF}(0,1) - c^\Gamma_{SI}(1)\right\|$	$\|c_{PF}(0,1) - c_{SI}(0,1)\|$
0.08	0.4	0.1191555	0.1175129
0.04	0.2	0.0685148	0.0682569
0.02	0.1	0.0383807	0.0384228
0.01	0.05	0.0209969	0.0210621
0.005	0.025	0.0114668	0.0115106
h	ε	$\max\|\gamma' - G'\|$	$\text{ave}\,\|\gamma' - G'\|$
0.08	0.4	0.5882511	0.1085532
0.04	0.2	0.3540145	0.0572062
0.02	0.1	0.2061245	0.0316161
0.01	0.05	0.1128733	0.0168467
0.005	0.025	0.0594562	0.0087458

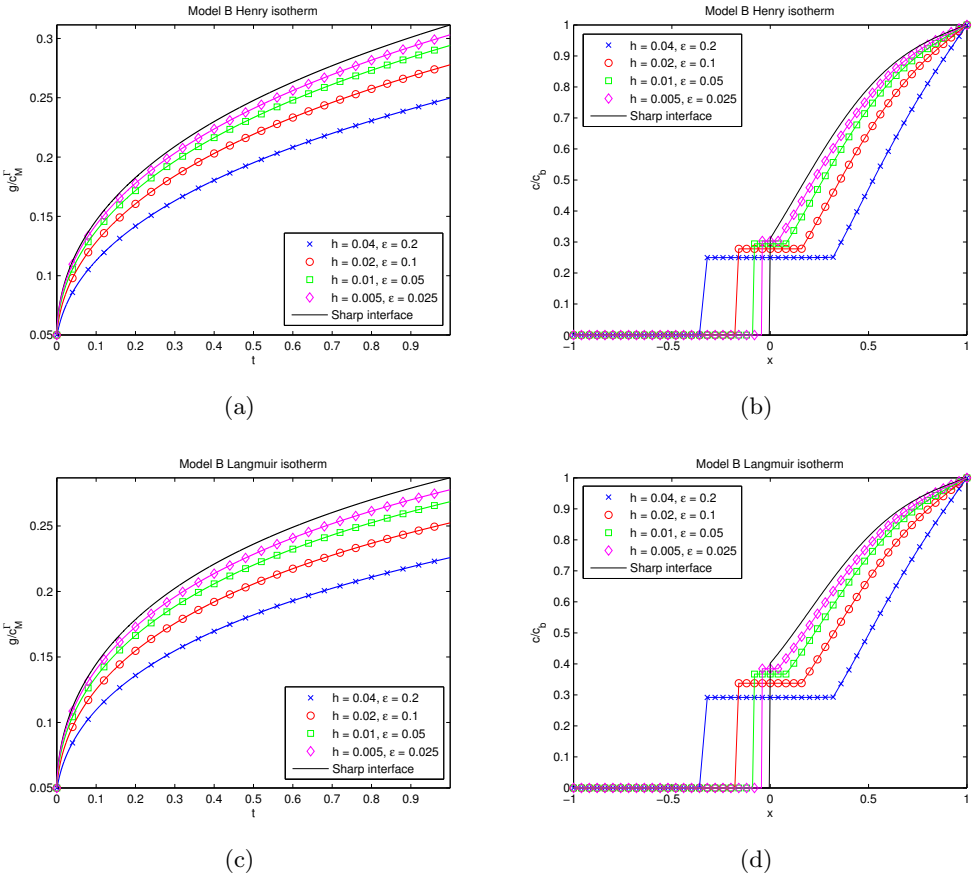
Table 4.2: Convergence table for Model A, instantaneous adsorption ($\alpha = \varepsilon$), Henry isotherm.

h	ε	$\left\|c^\Gamma_{PF}(0,1) - c^\Gamma_{SI}(1)\right\|$	$\|c_{PF}(0,1) - c_{SI}(0,1)\|$
0.08	0.4	0.0687143	0.1452171
0.04	0.2	0.0420765	0.0840548
0.02	0.1	0.0249919	0.0506682
0.01	0.05	0.0146093	0.0292756
0.005	0.025	0.0087232	0.0173523
h	ε	$\max\|\gamma' - G'\|$	$\text{ave}\,\|\gamma' - G'\|$
0.08	0.4	0.4014189	0.0759004
0.04	0.2	0.2347884	0.0389953
0.02	0.1	0.1326851	0.0210856
0.01	0.05	0.0711437	0.0110897
0.005	0.025	0.0370265	0.0057192

Table 4.3: Convergence table for Model A, instantaneous adsorption ($\alpha = \varepsilon$), Langmuir isotherm.

Numerics for Model B

For Model B, since we have instantaneous adsorption, we can infer the difference of $|c_{PF}(0,1) - c_{SI}(0,1)|$ from $\left|c^\Gamma_{PF}(0,1) - c^\Gamma_{SI}(1)\right|$ via the adsorption isotherms. Hence Table 4.4 displays only the difference $\left|c^\Gamma_{PF}(0,1) - c^\Gamma_{SI}(1)\right|$ for the Henry and Langmuir isotherms, in which we observe ε-convergence along with Figure 4.3. The model parameters are chosen to be the same as in Model A. From Tables 4.2 and



(a) (b)

(c) (d)

Figure 4.3: Model B ε-convergence for (a) the profile of $g(x = 0, t)$ and (b) the profile of $c(x, t = 1)$ with the Henry isotherm, (c) the profile of $g(x = 0, t)$ and (d) the profile of $c(x, t = 1)$ with the Langmuir isotherm.

4.4, the differences in Model B are smaller than those of Model A. So it appears that Model B performs better than Model A for the Henry isotherm (this may be due to the fact that the Henry isotherm transforms Model B into a linear equation, as demonstrated in Section 3.5.4). In contrast, from Tables 4.3 and 4.4, the differences in Model B are larger than those of Model A for all but the final iteration. But we have observed that the rate at which the error decreases is faster for Model B than for Model A in the Langmuir isotherm.

We leave a detailed comparison between Model A and Model B for instantaneous adsorption for future investigations, but we remark that for more complex isotherms, Model B will require a higher amount of computational effort relative to Model A due to the Newton iteration at each step. Since Model A with scaling $\alpha \sim \varepsilon$ works remarkably well, we recommend Model B only if one can afford the

higher computation cost.

h	ε	Henry	Langmuir
0.08	0.4	0.0938706	0.0895642
0.04	0.2	0.0616441	0.0593439
0.02	0.1	0.0336103	0.0330060
0.01	0.05	0.0172770	0.0168309
0.005	0.025	0.0083055	0.0076996

Table 4.4: Convergence table for Model B. Only the difference $\left|c^\Gamma_{PF}(0,1) - c^\Gamma_{SI}(1)\right|$ is displayed.

4.2.2 2D Simulations

In this section we present some results of numerical simulations in two spatial dimensions in order to qualitatively illustrate the effectivity of our approach. In a first setting we expose a droplet of a fluid suspended in another fluid to a shear flow. Under moderate shear rates the droplet's shape attains a steady state. This shape changes in the presence of the surfactant. Of particular interest to us is the dependence of the shape on the isotherm. In a second setting we start with a droplet at rest (in particular, in equilibrium with respect to the surfactant). Then we supply surfactant on one of the sides of the simulation box and investigate how far the droplet is sucked towards this side due to the Marangoni effect. As we are mainly interested in the effect of the surfactant on a qualitative basis we make convenient assumptions with respect to the two-phase flow, namely, that the fluids have the same mass densities and viscosities and that a Dirichlet boundary condition holds for the velocity. Also, the surfactant related parameters and data do not correspond to any specific species or systems.

Both dynamic adsorption (Model A) and instantaneous adsorption (Model C) have been considered. In both cases, the Navier-Stokes-Cahn-Hilliard system was solved following the lines of Kay, Styles, and Welford [2008] but we employed the double-obstacle potential for $W(\varphi)$. The saddle point problem arising from (3.5.3) and (3.5.5) has been solved with a preconditioned GMRES [Silvester et al., 2001]. For the phase field equation (3.5.6) together with (3.5.7) in form of a variational inequality we have employed a Gauss-Seidel type iteration as described in Barrett, Nürnberg, and Styles [2004].

For Model A, we always considered Fickian diffusion by setting $M^{(i)}_{c,*}(c_*) = 1/(G''_*(c_*)\mathrm{Pe}_{c,i})$ and $M_{\Gamma,*}(c^\Gamma_*) = 1/(\gamma''_*(c^\Gamma_*)\mathrm{Pe}_{\Gamma,i})$. We also replaced $\delta_*(\varphi, \nabla_*\varphi)$ by $2\mathcal{W}W(\varphi)/\varepsilon_*$ in the surfactant equation (3.5.9) which effects the validity of the energy

inequality but doesn't change the result of the asymptotic analysis. The reason is that the method developed in Elliott et al. [2011] can directly be applied. We leave a careful study of the impact of the gradient term for future investigations. In analogy to Elliott et al. [2011] a method for the degenerate bulk surfactant equations (3.5.8) has been developed. The methods have been implemented using the software ALBERTA, Version 2.0.1, [Schmidt and Siebert, 2005].

In the surfactant equation (3.5.10) for Model C we assumed constant mobilities, $M_{c,*}^{(i)}(c_*(q_*)) = 1/\mathrm{Pe}_{c,i}$ and $M_{\Gamma,*}(c_*^\Gamma(q_*)) = 1/\mathrm{Pe}_\Gamma$, and we also replaced $\delta_*(\varphi, \nabla_*\varphi)$ by $2\mathcal{W}W(\varphi)/\varepsilon_*$ for not having to deal with $\nabla_*\varphi$ in the diffusion term. Whenever no closed formula for c_*^Γ, $c_*^{(1)}$, or $c_*^{(2)}$ as a function of q_* was available we employed a Newton method. In the same way we also dealt with the nonlinear system of equations emerging from the finite element discretisation of the surfactant equation.

With regards to parameters and functions appearing in non-dimensional equations of the phase field models we have in both settings: $\mathcal{W} = \frac{2}{\pi}$, $\lambda_\rho = 1$, $\lambda_\eta = 1$, $\mathrm{Ca} = 0.1$,

$$\xi_1(\varphi) = \begin{cases} 1, & \text{if } 1 \leq \varphi, \\ \frac{1}{2}(\varphi + 1), & \text{if } -1 < \varphi < 1, \\ 0, & \text{if } \varphi \leq -1, \end{cases}$$

and $\xi_2(\varphi) = 1 - \xi_1(\varphi)$ where we set $\xi_i'(\varphi) = 0$ if $|\varphi| \geq 1$.

Droplet in shear flow

On the domain $\Omega = [-5, 5] \times [-2, 2] \subset \mathbb{R}^2$ the velocity was initialised with $\boldsymbol{v}(x_1, x_2, 0) = \mathbf{0}$. On the upper and lower boundary $\{x_2 = 2\}$ and $\{x_2 = -2\}$ we then increased the velocity linearly in time to $\boldsymbol{v}(x_1, x_2, t) = (x_2/2, 0)$, $t \geq 0.1$. On the two sides $\{x_1 = -5\}$ and $\{x_1 = 5\}$ we imposed the condition $\boldsymbol{v}(x_1, x_2, t) = \mathbf{0}$. The phase field was initialised with $\varphi(\boldsymbol{x}, 0) = \psi((\|\boldsymbol{x}\|_2 - 1)/\varepsilon)$, where

$$\psi(z) = \begin{cases} +1, & \text{if } z \geq \frac{\pi}{2}, \\ \sin(z), & \text{if } |z| < \frac{\pi}{2}, \\ -1, & \text{if } z \leq -\frac{\pi}{2}, \end{cases} \tag{4.2.8}$$

which yields a circular diffuse interface of radius one and centre $\boldsymbol{m} = (0, 0)$. Furthermore, we set $\mathrm{Re} = 0.1$ and $m_*(\varphi) = \frac{1}{2}(1 - \varphi^2)_+$.

We investigated Model A with $\mathrm{Pe}_\Gamma = 2.5$, $\mathrm{Pe}_{c,i} = 2.5$, and $\alpha_*^{(i)} = 1$ for $i = 1, 2$ for the following isotherms (assuming the same free energies in the two bulk phases,

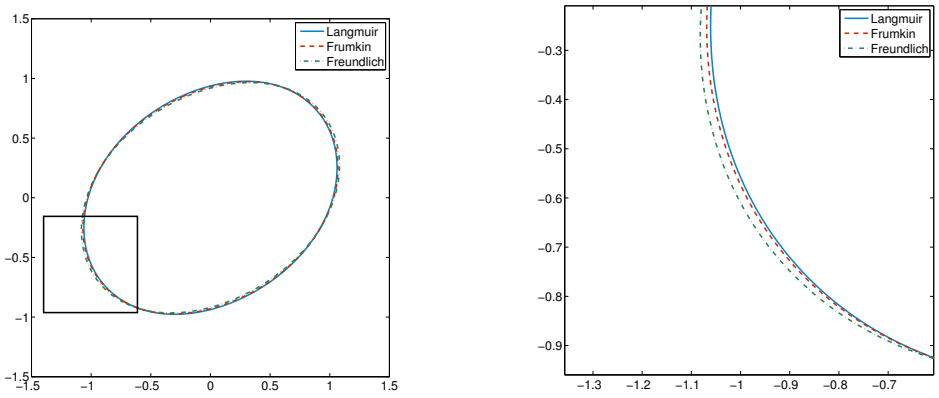


Figure 4.4: Droplet in shear flow: Zero level sets of φ for several isotherms, $\varepsilon = 0.0565685425 \approx 0.08/\sqrt{2}$, $t = 10$. The right graph displays a zoom into the square indicated on the left graph.

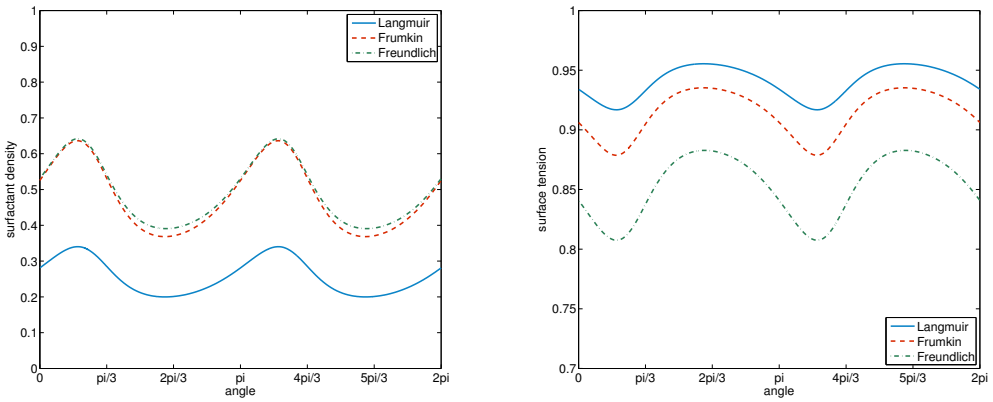


Figure 4.5: Droplet in shear flow: Interface surfactant density c_*^Γ (left) and surface tension $\sigma_*(c_*^\Gamma)$ (right) plotted over the angle formed by the line from the centre to a boundary point and the x-axis for several isotherms, $\varepsilon = 0.0565685425 \approx 0.08/\sqrt{2}$, $t = 10$.

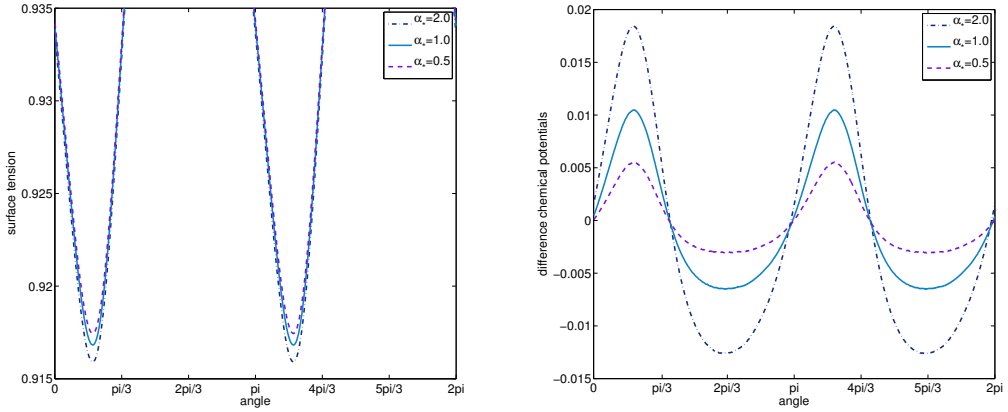


Figure 4.6: Droplet in shear flow: Surface tension $\sigma_*(c_*^\Gamma)$ at the tips of the droplet (left) and difference of surface and bulk chemical potentials $\gamma_*'(c_*^\Gamma) - G_*'(c_*^{(2)})$ (right) plotted over the angle formed by the line from the centre to a boundary point and the x-axis for several values of α_*, $\varepsilon = 0.0565685425 \approx 0.08/\sqrt{2}$, $t = 10$.

thus dropping the index):

- Langmuir ($B = 0.2$, $\sigma_0 = 1$, $K = 10$);
- Frumkin ($B = 0.2$, $\sigma_0 = 1$, $K = 10$, $A = 0.4$);
- Freundlich ($B = 0.2$, $\sigma_0 = 1$, $K = 10$, $N = 1.5$, $A_c = 1.0$).

The initial bulk surfactant density was $c_*^{(1)} = c_*^{(2)} = 1/(10e) \approx 0.03679$, and the interfacial surfactant density c_*^Γ was the equilibrium value (thus, depending on the isotherm).

At time $t = 10$ the droplets seemed to have attained stationary shapes. These are displayed in Figure 4.4 for several isotherms. For our parameters we found that the Langmuir isotherm leads to the least deformed shape while the shape for the Freundlich isotherm is most deformed when comparing with the initial circular shape. A common measure for the deformation is the Taylor deformation parameter $D_{Tay} = (L-B)/(L+B)$ where L and B are the maximum and the minimum distance to the centre, respectively. We obtained the following values:

isotherm	Langmuir	Frumkin	Freundlich
D_{Tay}	0.143298	0.148370	0.160821

In Figure 4.5 we display the surface surfactant density and the surface tension along the interface between the two fluids which qualitatively reveal the usual distribution, for instance, compare with Lai, Tseng, and Huang [2008].

We also investigated a change in the adsorption parameter $\alpha_*^{(i)}$ (both always equal for the two phases, whence we drop the upper index). The impact on the shape is small in comparison with the isotherm. For the Langmuir isotherm, we obtained the deformation parameters:

adsorption parameter	$\alpha_* = 2.0$	$\alpha_* = 1.0$	$\alpha_* = 0.5$
D_{Tay}	0.143395	0.143298	0.143241

In Figure 4.6 the difference of the chemical potentials at the interface is displayed, revealing the expected convergence to zero when the adsorption parameter α_* decreases.

Marangoni effect

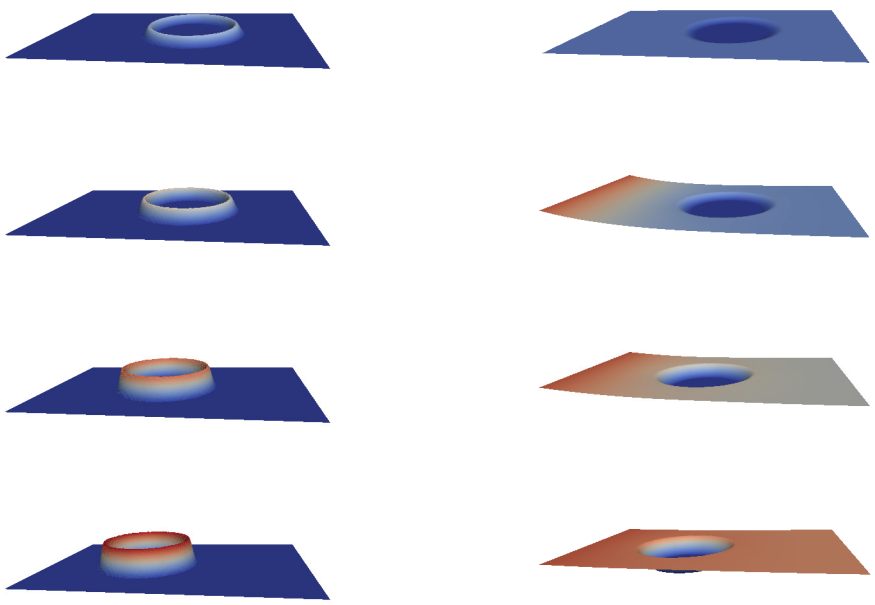


Figure 4.7: Marangoni effect on a surfactant laden droplet due to the provision of surfactant at the boundary. Computed fields $2W(\varphi)c_*^\Gamma(q_*)$ (left) and $\xi_1(\varphi)c_*^{(1)}(q_*)$ (right) are plotted over the domain $\Omega = [-3,3] \times [-2,2]$ (x-axis from left to right, y-axis from front to rear, z-axis or height indicates the value of the field) at times $t = 0, 10, 40, 100$ (top down) for a simulation performed with the Frumkin isotherm data (see Section 4.2.2) and $\varepsilon = 0.12$. The data range is between 0.0 (blue) and about 0.585 (red).

We now consider the domain $\Omega = [-3,3]\times[-2,2]$. Both velocity and pressure are initialised with 0, and this is also the Dirichlet boundary condition for the velocity. For the phase field we set $\varphi(\boldsymbol{x},0) = \psi((\|\boldsymbol{x}-\boldsymbol{m}\|_2 - 1)/\varepsilon)$, with ψ given as in 4.2.8, and $\boldsymbol{m} = (0.5, 0)$, which corresponds to a circular diffuse interface of radius one around $\boldsymbol{m}$. The Reynolds number is $\mathrm{Re} = 10$ and we chose $m_*(\varphi) = (1-\varphi^2)_+$.

Simulations were performed with Model C where we set $\mathrm{Pe}_{c,i} = \mathrm{Pe}_\Gamma = 10.0$, $i = 1, 2$ and used the following free energies (again, the free energies in the two bulk phases are assumed to be the same so that the index is dropped):

- Langmuir ($B = 1$, $\sigma_0 = 2$, $K = 2.5$);
- Frumkin ($B = 1$, $\sigma_0 = 2$, $K = 2.5$, $A = 0.4$);
- Freundlich ($B = 1$, $\sigma_0 = 2$, $K = 1$, $N = 1.5$, $A_c = 0.6$).

The field q_* was initialised such that $c_*^{(1)}(q_*) = c_*^{(2)}(q_*) = 0.1$. During the time interval $[0, 0.1]$ we linearly increased q_* on the boundary $\{x_1 = -3\}$ such that, at $t = 0.1$, $c_*^{(1)}(q_*) = 0.5$.

As a consequence, the droplet moved in $-x_1$ direction towards the source of the surfactant as exemplary illustrated in Figure 4.7 for the Frumkin isotherm data. Initially at rest, the supply of surfactant on the boundary leads to a surfactant gradient at the interface of the droplet. Since σ_* is decreasing in c_*^Γ the related Marangoni force $\nabla_\Gamma \sigma_*(c_*^\Gamma)$ points into the opposite direction and, thus, leads to a drift towards the source of the surfactant. In the long term, the system reaches a steady state again with spatially homogeneous distributions of the surfactant in both phases and on the interface, which is fairly achieved at time $t = 100.0$. For our choice of parameters the Freundlich isotherm lead to the most significant displacement d_{x_1} along the x_1 axis while the Langmuir isotherm lead to the least significant displacement:

	Langmuir	Frumkin	Freundlich
d_{x_1}	-1.055512	-1.087783	-1.114869

Chapter 5

Diffuse interface approximations for linear elliptic PDEs

5.1 Introduction

The diffuse domain approach is a method originating from the phase field methodology which approximates partial differential equations posed on domains with arbitrary geometries. Similar to the fictitious domain method, the diffuse domain method embeds the original domain $\Omega^{(1)}$ with the complicated geometries into a larger domain Ω with a simpler geometry. Drawing on aspects of the phase field methodology, the diffuse domain method replaces the boundary Γ of $\Omega^{(1)}$ with an interfacial layer of thickness $0 < \varepsilon \ll 1$, denoted by Γ_ε. The original PDEs posed on $\Omega^{(1)}$ will have to be extended to Ω and any surface quantities or boundary terms on Γ have to be extended to fields defined on Γ_ε. The resulting PDE system, which we denote as the diffuse domain approximation, is defined on Ω and will have the same order as the original system defined in $\Omega^{(1)}$, but with additional lower order terms that approximate the original boundary conditions on Γ.

In this chapter, we study the model coupled bulk-surface system:

$$\text{(CSI)} \quad \begin{aligned} -\nabla \cdot (\mathcal{A}\nabla u) + au &= f, \text{ in } \Omega^{(1)}, \\ -\nabla_\Gamma \cdot (\mathcal{B}\nabla_\Gamma v) + bv + \mathcal{A}\nabla u \cdot \nu &= \beta g, \text{ on } \Gamma, \\ \mathcal{A}\nabla u \cdot \nu &= K(v - \gamma_0(u)), \text{ on } \Gamma. \end{aligned}$$

Here, $\gamma_0 : W^{1,1}(\Omega) \to L^1(\Gamma)$ is the Boundary-Trace mapping (Theorem C.3), $K, \beta \geq 0$ are non-negative constants and $\mathcal{A} = (a_{ij})_{1\leq i,j\leq n}, \mathcal{B} = (b_{ij})_{1\leq i,j\leq n}$ for functions $a_{ij} : \Omega^{(1)} \to \mathbb{R}$ and $b_{ij} : \Gamma \to \mathbb{R}$.

We embed $\Omega^{(1)} \cup \Gamma$ into a larger domain Ω. The location of the original boundary Γ is encoded in an order parameter φ as its zero-level set. A typical choice for φ is based on the signed distance function, $d : \Omega \to \mathbb{R}$, of Γ defined as

$$d(x) = \begin{cases} -\text{dist}(x, \Gamma), & \text{for } x \in \Omega^{(1)}, \\ 0, & \text{for } x \in \Gamma, \\ \text{dist}(x, \Gamma), & \text{for } x \in \Omega \setminus \overline{\Omega^{(1)}}, \end{cases} \tag{5.1.1}$$

where

$$\text{dist}(x, \Gamma) = \inf \left\{ \int_0^1 \left\| \gamma'(s) \right\| ds : \gamma \in C^1([0,1], \overline{\Omega}), \gamma(0) = x, \gamma(1) \in \Gamma \right\}.$$

Let $\chi_{\Omega^{(1)}}$ and δ_Γ formally denote the distributions given by the Dirac measures of $\Omega^{(1)}$ and Γ, respectively. By Theorem B.1, an equivalent distributional form for (CSI) is

$$\begin{aligned} -\nabla \cdot (\chi_{\Omega^{(1)}} \mathcal{A} \nabla u) + \chi_{\Omega^{(1)}} a u &= \chi_{\Omega^{(1)}} f + \delta_\Gamma K(v - \gamma_0(u)), \\ -\nabla \cdot (\delta_\Gamma \mathcal{B} \nabla v) + \delta_\Gamma b v &= \delta_\Gamma \beta g - \delta_\Gamma K(v - \gamma_0(u)). \end{aligned}$$

The diffuse domain approximation of (CSI) is derived by approximating $\chi_{\Omega^{(1)}}$ and δ_Γ with more regular functions $\xi_\varepsilon(\varphi), \delta_\varepsilon(\varphi)$, indexed by ε, the width of the interfacial layer Γ_ε. In other words, a diffuse domain approximation of (CSI) is

$$\text{(CDD)} \qquad \begin{aligned} -\nabla \cdot (\xi_\varepsilon \mathcal{A}^E \nabla u^\varepsilon) + \xi_\varepsilon a^E u^\varepsilon &= \xi_\varepsilon f^E + \delta_\varepsilon K(v^\varepsilon - u^\varepsilon), \text{ in } \Omega, \\ -\nabla \cdot (\delta_\varepsilon \mathcal{B}^E \nabla v^\varepsilon) + \delta_\varepsilon b^E v^\varepsilon &= \delta_\varepsilon \beta g^E - \delta_\varepsilon K(v^\varepsilon - u^\varepsilon), \text{ in } \Omega, \end{aligned}$$

where terms with superscript E denote extensions to the larger domain Ω. Formally, $\xi_\varepsilon(\varphi) \to \chi_{\Omega^{(1)}}, \delta_\varepsilon(\varphi) \to \delta_\Gamma$ pointwise as $\varepsilon \to 0$, and so in the limit of vanishing interfacial thickness, we recover the distributional form for (CSI).

The phase field methodology provides us with two candidates for $\varphi(x)$. The first is based on the smooth double-well potential $\psi_{DW}(\varphi) = \frac{1}{4}(1 - \varphi^2)^2$ and leads to

$$\varphi_{DW}(x) := \tanh\left(\frac{d(x)}{\sqrt{2}\varepsilon}\right).$$

The other is based on the double-obstacle potential

$$\psi_{DO}(\varphi) = \frac{1}{2}(1-\varphi^2) + I_{[-1,1]}(\varphi), \quad I_{[-1,1]}(\varphi) = \begin{cases} 0, & \text{if } \varphi \in [-1,1], \\ +\infty, & \text{otherwise,} \end{cases}$$

and leads to

$$\varphi_{DO}(x) := \begin{cases} +1, & \text{if } d(x) > \varepsilon\frac{\pi}{2}, \\ \sin(d(x)/\varepsilon), & \text{if } |d(x)| \leq \varepsilon\frac{\pi}{2}, \\ -1, & \text{if } d(x) < -\varepsilon\frac{\pi}{2}. \end{cases}$$

We remark that φ_{DW} or φ_{DO} is the leading order approximation for the order parameter φ in general phase field models, as seen in Chapter 4. In our setting, the location of the boundary Γ is known and hence we can use φ_{DW} or φ_{DO} as the order parameter. A common regularisation of $\chi_{\Omega^{(1)}}$ based on the smooth double-well potential used in Li et al. [2009]; Teigen et al. [2009, 2011] is

$$\xi_\varepsilon^{(1)}(x) = \frac{1}{2}(1-\varphi_{DW}(x)) = \frac{1}{2}\left(1 - \tanh\left(\frac{d(x)}{\sqrt{2}\varepsilon}\right)\right).$$

While an alternative based on the double-obstacle potential is

$$\xi_\varepsilon^{(2)}(x) = \frac{1}{2}(1-\varphi_{DO}(x)).$$

There are many regularisations of δ_Γ available from the literature Teigen et al. [2011]; Elliott et al. [2011]; Rätz and Voigt [2006]; Lee and Junseok [2012]. We will use the Ginzburg–Landau energy density $\delta(\varphi, \nabla\varphi)$ as defined in (3.2.1) as our regularisation for δ_Γ. From the above discussions regarding the double-well and the double-obstacle potentials, and also from Chapter 4, we have two candidates for the regularisation to δ_Γ:

$$\delta_\varepsilon^{(1)}(x) = \frac{3}{2\sqrt{2}\varepsilon}\operatorname{sech}^4(d(x)/(\sqrt{2}\varepsilon)), \quad \delta_\varepsilon^{(2)}(x) = \frac{2}{\pi\varepsilon}\cos^2(d(x)/\varepsilon)\mathbb{I}_{\{x\in\Omega\,:\,|d(x)|\leq\varepsilon\frac{\pi}{2}\}}.$$

The convergence analysis of the diffuse domain approach (with the smooth double-well potential), in the limit $\varepsilon \to 0$, has only been done in the context of recovering the original equations via formally matched asymptotics (see Li et al. [2009]; Teigen et al. [2009, 2011]). A first analytical treatment of convergence in one dimension and on a half-plane in two dimension can be found in Franz et al. [2012], where the error between the solution to a second order system and the diffuse

domain approximation in the L^∞ norm is of order $\mathcal{O}(\varepsilon^{1-\mu})$, where $\mu > 0$ is arbitrary small.

In Elliott and Stinner [2009], a diffuse domain type approximation for an advection-diffusion equation posed on evolving surfaces is considered. Motivated by modelling and numerical simulations, the diffuse domain approximation utilises a double-obstacle type regularisation. Note that the regularisations from the double-obstacle potential are degenerate in certain parts of the larger domain Ω (in particular they are zero outside Γ_ε). Consequently the corresponding diffuse domain approximation becomes a degenerate equation and weighted Sobolev spaces are employed. The chief results in Elliott and Stinner [2009] are the well-posedness of the diffuse domain approximation and weak convergence to the solution of the original system.

In this chapter, we extend the analysis of Franz et al. [2012] to cover the regularisations that originate from double-obstacle potential and any dimension $n \geq 1$. For (CSI) we show strong convergence for the bulk quantity, and norm convergence for the surface quantity. The techniques for analysing the surface quantities are motivated from the analysis of Elliott and Stinner [2009], but the advantage of our method is that we do not need to parameterise the hypersurface.

5.2 General assumptions and main results

5.2.1 Assumptions

Assumption 5.1 (Assumptions on domain)**.** *We assume that $\Omega^{(1)}$ is an open bounded domain in $\mathbb{R}^n$ with compact C^3 boundary Γ and outward unit normal ν. Let Ω be an open bounded domain in $\mathbb{R}^n$ with Lipschitz boundary $\partial\Omega$ such that $\overline{\Omega^{(1)}} \subset \Omega$ and $\Gamma \cap \partial\Omega = \emptyset$. Furthermore we assume that for any finite open covering $\{W_i \cap \Gamma\}_{i=1}^N, W_i \subset \mathbb{R}^n$ of Γ there exists a corresponding local regular parameterisation $\alpha_i : \mathcal{S}_i \subset \mathbb{R}^{n-1} \to W_i \cap \Gamma$.*

Assumption 5.2 (Assumptions for (CSI))**.** *We assume that for $1 \leq i, j \leq n$,*

$$a_{ij}, a \in L^\infty(\overline{\Omega^{(1)}}), \quad f \in L^2(\Omega^{(1)}), \quad b_{ij}, b \in L^\infty(\Gamma), \quad g \in L^2(\Gamma),$$

and there exist positive constants $\theta_0, \theta_1, \theta_2, \theta_3$ such that

$$(\mathcal{A}(x)\zeta_1) \cdot \zeta_1 \geq \theta_0 |\zeta_1|^2, \quad (\mathcal{B}(p)\zeta_2) \cdot \zeta_2 \geq \theta_1 |\zeta_2|^2, \quad a(x) \geq \theta_2, \quad b(p) \geq \theta_3 \geq K,$$

for all $x \in \Omega^{(1)}$, $p \in \Gamma$, $\zeta_1 \in \mathbb{R}^n$ and $\zeta_2 \in T_p\Gamma \subset \mathbb{R}^n$.

We observe that setting $\mathcal{A} = \mathbf{0}$, $a = 0$, $f = 0$, $K = 0$, $\beta = 1$ in (CSI) leads to an elliptic equation on Γ, which we denote as (SSI):

$$\text{(SSI)} \quad -\nabla_\Gamma \cdot (\mathcal{B}\nabla_\Gamma v) + bv = g, \text{ on } \Gamma.$$

Meanwhile, setting $\mathcal{B} = \mathbf{0}$, $b(x) \equiv \beta$ and formally sending K to ∞ in (CSI) leads to the Robin boundary condition (RSI):

$$\text{(RSI)} \quad \begin{aligned} -\nabla \cdot (\mathcal{A}\nabla u) + au &= f, \text{ in } \Omega, \\ \mathcal{A}\nabla u \cdot \nu + \beta\gamma_0(u) &= \beta g, \text{ on } \Gamma. \end{aligned}$$

Formally sending $K \to \infty$, setting $v = g$ and neglecting the second equation in (CSI) gives the Dirichlet boundary condition (DSI):

$$\text{(DSI)} \quad \begin{aligned} -\nabla \cdot (\mathcal{A}\nabla u) + au &= f, \text{ in } \Omega, \\ \gamma_0(u) &= g, \text{ on } \Gamma, \end{aligned}$$

while the Neumann boundary condition (NSI) can be obtained by setting $\mathcal{B} = 0$, $b = 0$, $\beta = 1$ and neglecting the last boundary condition in (CSI):

$$\text{(NSI)} \quad \begin{aligned} -\nabla \cdot (\mathcal{A}\nabla u) + au &= f, \text{ in } \Omega, \\ \mathcal{A}\nabla u \cdot \nu &= g, \text{ on } \Gamma. \end{aligned}$$

In order to cover these derived elliptic problems in our analysis, we make the following specific assumptions:

Assumption 5.3 (Specific assumptions)**.** *In addition to Assumptions 5.1 and 5.2, we assume that if $g \neq 0$, then*

- *for (DSI), $g \in H^{\frac{1}{2}}(\Gamma)$;*
- *for (NSI), $g \in H^{\frac{1}{2}}(\Gamma)$, and for $1 \leq i, j \leq n$, there exist two constants m, M such that $0 < m \leq M$ and*

$$a_{ij} \in C^\infty(\overline{\Omega^{(1)}}), \quad m \leq \Big| \sum_{j=1}^{n} a_{ij}(x)\nu_j(x) \Big| \leq M \text{ a.e. on } \Gamma.$$

Moreover, for (RSI), (DSI) and (NSI), we only require $\Omega^{(1)}$ to be an open bounded domain with C^2 boundary Γ.

We remark that under Assumption 5.3, we can transform (DSI) and (NSI) into their homogeneous counterparts: If $g \in H^{\frac{1}{2}}(\Gamma)$, then by Theorem C.6, there

exists $\tilde{g} \in H^1(\Omega^{(1)})$ such that $\gamma_0(\tilde{g}) = g$, and (DSI) is equivalent to the following homogeneous problem (DSIH):

$$\text{(DSIH)} \qquad \begin{aligned} -\nabla \cdot (\mathcal{A}\nabla w) + aw &= f + \nabla \cdot (\mathcal{A}\nabla \tilde{g}) - a\tilde{g}, \text{ in } \Omega^{(1)}, \\ \gamma_0(w) &= 0, \text{ on } \Gamma. \end{aligned}$$

If w is a weak solution of (DSIH) then $u := w + \tilde{g}$ is a weak solution of (DSI).

Similarly, if $g \in H^{\frac{1}{2}}(\Gamma)$ and $\mathcal{A}$ satisfy the assumptions of Theorem C.7, then there exists $\hat{g} \in H^2(\Omega^{(1)})$ such that $\mathcal{A}\nabla\hat{g} \cdot \nu = g$. Thus, (NSI) is equivalent to the following homogeneous problem (NSIH):

$$\text{(NSIH)} \qquad \begin{aligned} -\nabla \cdot (\mathcal{A}\nabla w) + aw &= f + \nabla \cdot (\mathcal{A}\nabla \hat{g}) - a\hat{g}, \text{ in } \Omega^{(1)}, \\ \mathcal{A}\nabla w \cdot \nu &= 0, \text{ on } \Gamma, \end{aligned}$$

where $u := w + \hat{g}$ is a weak solution to (NSI).

We remark that the assumption $g \in H^{\frac{1}{2}}(\Gamma)$ is required for the well-posedness of (DSI), while the convergence analysis of the diffuse domain approximation for (NSI) requires Assumption 5.3 (see the discussion in Section 5.4.3). Moreover, the C^3 boundary assumption is needed for the approximation of surface gradients (see Lemma 5.26), while a C^2 boundary is the minimum requirement for the technical results in Sections 5.3.1 and 5.3.2 to apply.

Similarly, by Theorem B.1, the corresponding diffuse domain approximations for (SSI), (RSI) and (NSIH) are

$$\begin{aligned} \text{(SDD)} \quad & -\nabla \cdot (\mathcal{B}^E \delta_\varepsilon \nabla u^\varepsilon) + \delta_\varepsilon b^E u^\varepsilon = \delta_\varepsilon g^E, && \text{in } \Omega, \\ \text{(RDD)} \quad & -\nabla \cdot (\mathcal{A}^E \xi_\varepsilon \nabla u^\varepsilon) + \xi_\varepsilon a^E u^\varepsilon + \beta \delta_\varepsilon u^\varepsilon = \xi_\varepsilon f^E + \beta \delta_\varepsilon g^E, && \text{in } \Omega, \\ \text{(NDDH)} \quad & -\nabla \cdot (\mathcal{A}^E \xi_\varepsilon \nabla w^\varepsilon) + a^E \xi_\varepsilon w^\varepsilon = \xi_\varepsilon f^E + \xi_\varepsilon \nabla \cdot (\mathcal{A}^E \nabla \hat{g}^E) - a^E \xi_\varepsilon \hat{g}^E, && \text{in } \Omega, \end{aligned}$$

We remark that the Dirichlet boundary condition is not covered in Theorem B.1. One way to achieve this is to see the Dirichlet condition as a limiting condition from the homogeneous Robin condition when $\beta \to +\infty$ (see Marušić-Paloka [1999] or Lemma 5.10 below). Hence, a diffuse domain approximation to (DSIH) is

$$\text{(DDDH)} \quad -\nabla \cdot (\mathcal{A}^E \xi_\varepsilon \nabla w^\varepsilon) + a^E \xi_\varepsilon w^\varepsilon + \frac{1}{\varepsilon} \delta_\varepsilon w^\varepsilon = \xi_\varepsilon f^E + \nabla \cdot (\mathcal{A}^E \xi_\varepsilon \nabla \tilde{g}^E) - \xi_\varepsilon a^E \tilde{g}^E.$$

We impose the zero Neumann boundary condition for our diffuse domain approxi-

mations:

$$\mathcal{A}^E \nabla u^\varepsilon \cdot \nu_{\partial\Omega} = \mathcal{B}^E \nabla v^\varepsilon \cdot \nu_{\partial\Omega} = 0 \text{ on } \partial\Omega.$$

5.2.2 Extensions of the data

Since there is no unique extension operator for L^p functions, we make the following assumption:

Assumption 5.4 (Assumptions on bulk extended data)**.** *Let $1 \leq i, j \leq n$. We assume that $(\mathcal{A}^E)_{ij}, a^E \in L^\infty(\Omega)$ and $f^E \in L^2(\Omega)$ are extensions of $(\mathcal{A})_{ij}, a \in L^\infty(\overline{\Omega^{(1)}})$ and $f \in L^2(\Omega^{(1)})$, respectively, such that $\mathcal{A}^E$ is uniformly elliptic with constant θ_0 and $a^E(x) \geq \theta_2$ for a.e. $x \in \Omega$.*

If $f \in W^{l,p}(\Omega^{(1)})$ for some $l \geq 1$, then one can use an order $l-1$ reflection about the boundary Γ to extend f into the exterior of $\Omega^{(1)}$. For the case $l = 1$, this is outlined in the Extension theorem (Theorem C.2). For higher order reflections, we refer to Theorem 5.19, pg. 148 of Adams and Fournier [2003] or pg. 43-44 of Maz'ja and Poborchi [1997].

For the Dirichlet problem with any $g \in H^{\frac{1}{2}}(\Gamma)$, we use Theorem C.6 to deduce the existence of $\tilde{g} \in H^1(\Omega^{(1)})$ such that $\gamma_0(\tilde{g}) = g$. We then extend $\tilde{g} \in H^1(\Omega^{(1)})$ to a function $\tilde{g}^E \in H^1(\Omega)$ by Theorem C.2.

For the Neumann problem, by Theorem C.7, we can find $\hat{g} \in H^2(\Omega^{(1)})$ such that $\mathcal{A}\nabla\hat{g} \cdot \nu = g$. By the reflection method, we can extend $\hat{g}$ to a function $\hat{g}^E \in H^2(\Omega)$.

5.2.3 Constant extension in the normal direction

We define the tubular neighbourhood $\text{Tub}^r(\Gamma)$ of Γ with width $r > 0$ as

$$\text{Tub}^r(\Gamma) := \{x \in \Omega : |d(x)| < r\}.$$

Then, by Lemma 14.16 of Gilbarg and Trudinger [1983], there exists $\eta > 0$ such that the signed distance function d to Γ is of class $C^3(\text{Tub}^\eta(\Gamma))$ and is globally Lipschitz with constant 1 (see Section 14.6 of Gilbarg and Trudinger [1983]).

For each $y \in \Gamma$, denote its tangent space by $T_y\Gamma$ and its outward pointing unit normal by $\nu(y)$. A standard result in differential geometry shows that for η sufficiently small, there is a diffeomorphism between $\text{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. For any $x \in \text{Tub}^\eta(\Gamma)$, we define the closest point operator (see Merriman and Ruuth

[2007] or Lemma 2.8 of Dziuk and Elliott [2013]) $p : \mathrm{Tub}^{\eta}(\Gamma) \to \Gamma$ by

$$x = p(x) + d(x)\nu(p(x)). \tag{5.2.1}$$

Moreover, the signed distance function d satisfies

$$\nabla d(x) = \nu(p(x)) \text{ for } x \in \mathrm{Tub}^{\eta}(\Gamma). \tag{5.2.2}$$

For any $g \in L^p(\Gamma)$, $1 \leq p \leq \infty$, we define its constant extension g^e off Γ in the normal direction as

$$g^e(x) = g(p(x)) \text{ for all } x \in \mathrm{Tub}^{\eta}(\Gamma). \tag{5.2.3}$$

Then, $g^e \in L^p(\mathrm{Tub}^{\eta}(\Gamma))$ and we let $g^E \in L^p(\Omega)$ be an extension of g^e from $\mathrm{Tub}^{\eta}(\Gamma)$ to Ω. Analogous to the extensions of bulk data, we make the following assumption:

Assumption 5.5 (Assumptions on surface extended data)**.** *Let $1 \leq i, j \leq n$. We assume that $(\mathcal{B}^E)_{ij}, b^E \in L^\infty(\Omega)$ and $g^E \in L^2(\Omega)$ are extensions of $(\mathcal{B})_{ij}, b \in L^\infty(\Gamma)$ and $g \in L^2(\Gamma)$ constantly in the normal direction, such that $\mathcal{B}^E$ is uniformly elliptic with constant θ_1 and $b^E(x) \geq \theta_3$ for a.e. $x \in \Omega$.*

In the subsequent sections, we associate $g^E \in L^2(\Omega)$ in (CDD), (SDD) and (RDD) with the constant extension of $g \in L^2(\Gamma)$ in the normal direction, while $\tilde{g}^E \in H^1(\Omega)$ and $\hat{g}^E \in H^2(\Omega)$ in (DDDH) and (NDDH) are associated with the extensions of $\tilde{g} \in H^1(\Omega^{(1)})$ and $\hat{g} \in H^2(\Omega^{(1)})$, respectively.

5.2.4 Assumptions on regularisations of indicator functions

We first introduce the functions ξ and δ, from which the regularisations ξ_ε and δ_ε are constructed by a rescaling.

Assumption 5.6. *We assume that $\xi : \mathbb{R} \to [0, 1]$ is a C^1, nonnegative, monotone function such that,*

$$\lim_{\varepsilon \to \infty} \xi\Big(\frac{x}{\varepsilon}\Big) = \begin{cases} 1, & \text{if } x < 0, \\ 0, & \text{if } x > 0, \\ \frac{1}{2}, & \text{if } x = 0, \end{cases} \tag{5.2.4}$$

and

$$\xi^{-1} \in L^1_{loc}(\{x \in \mathbb{R} : \xi(x) > 0\}).$$

Assumption 5.7. *We assume that $\delta : \mathbb{R} \to [0,1]$ is a C^1, nonnegative even function such that*

$$\int_{\mathbb{R}} \delta(s)\, ds = 1, \quad \delta(s_1) \geq \delta(s_2) \text{ if } |s_1| \leq |s_2|, \quad \delta^{-1} \in L^1_{loc}(\{x \in \mathbb{R} : \delta(x) > 0\}),$$
$$\int_{\mathbb{R}} \frac{|\delta'(s)|^2}{\delta(s)}\, ds + \int_{\mathbb{R}} \sqrt{\delta(s)}\, ds + \int_0^\infty \delta(s) s\, ds =: C_{\delta,\text{int}} < \infty, \tag{5.2.5}$$

and for any $q_1 \geq q_2 > 0$,

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon^{q_1}} \delta\left(\frac{x}{\varepsilon^{q_2}}\right) = \begin{cases} 0, & \text{if } x \neq 0, \\ +\infty, & \text{if } x = 0. \end{cases} \tag{5.2.6}$$

Moreover, we assume there exists a constant $C_\xi > 0$ such that

$$C_\xi \delta(t) \leq \xi(t) \text{ for all } t \in \mathbb{R}. \tag{5.2.7}$$

Definition 5.8. Let $d(x)$ denote the signed distance function to Γ. For each $\varepsilon \in (0,1]$, we define ξ_ε and δ_ε as

$$\xi_\varepsilon(x) := \xi\Big(\frac{d(x)}{\varepsilon}\Big), \quad \delta_\varepsilon(x) := \frac{1}{\varepsilon}\delta\Big(\frac{d(x)}{\varepsilon}\Big) \quad \text{for } x \in \Omega, \tag{5.2.8}$$

with

$$\Omega_\varepsilon := \{x \in \Omega : \xi_\varepsilon(x) > 0\}, \quad \Gamma_\varepsilon := \{x \in \Omega : \delta_\varepsilon(x) > 0\}.$$

By (5.2.7), (5.2.4), and (5.2.6), we observe that

$$\Omega^{(1)} \cup \Gamma \subset \Omega_\varepsilon, \quad \Gamma \subset \Gamma_\varepsilon \subset \Omega_\varepsilon \quad \text{for all } \varepsilon > 0.$$

One can check that our candidate regularisation originating from the double-well potential:

$$\xi^{(1)}_\varepsilon(x) := \frac{1}{2}\left(1 - \tanh\left(\frac{d(x)}{\sqrt{2}\varepsilon}\right)\right), \quad \delta^{(1)}_\varepsilon(x) := \frac{3}{2\sqrt{2}\varepsilon}\operatorname{sech}^4\left(\frac{d(x)}{\sqrt{2}\varepsilon}\right), \tag{5.2.9}$$

and regularisation originating from the double-obstacle potential:

$$\begin{aligned} \xi^{(2)}_\varepsilon(x) &:= \mathbb{I}_{\{x\in\Omega\,:\,d(x)<-\varepsilon\frac{\pi}{2}\}} + \frac{1}{2}\left(1 - \sin\left(\frac{d(x)}{\varepsilon}\right)\right)\mathbb{I}_{\{x\in\Omega\,:\,|d(x)|\leq\varepsilon\frac{\pi}{2}\}}, \\ \delta^{(2)}_\varepsilon(x) &:= \frac{2}{\pi\varepsilon}\cos^2\left(\frac{d(x)}{\varepsilon}\right)\mathbb{I}_{\{x\in\Omega\,:\,|d(x)|\leq\varepsilon\frac{\pi}{2}\}}, \end{aligned} \tag{5.2.10}$$

satisfy Assumptions 5.6 and 5.7.

5.2.5 Main results

For convenience, let us define:

$$a_B(\varphi,\psi) := \int_{\Omega^{(1)}} \mathcal{A}\nabla\varphi\cdot\nabla\psi + a\varphi\psi\,dx, \quad l_B(\varphi,\psi) := \int_{\Omega^{(1)}} \varphi\psi\,dx,$$
$$a_S(\varphi,\psi) := \int_{\Gamma} \mathcal{B}\nabla_\Gamma\varphi\cdot\nabla_\Gamma\psi + b\varphi\psi\,d\mathcal{H}, \quad l_S(\varphi,\psi) := \int_{\Gamma} \varphi\psi\,d\mathcal{H},$$

where $d\mathcal{H}$ denotes the $n-1$ dimensional Hausdorff measure.

Theorem 5.9 (Well-posedness for the original problems)**.** *Suppose the data satisfy Assumptions 5.1, 5.2, and 5.3. Then there exist unique weak solutions*

$$(u,v) \in H^1(\Omega^{(1)})\times H^1(\Gamma) \text{ for (CSI)},$$
$$v_S \in H^1(\Gamma) \text{ for (SSI)}, \quad u_R \in H^1(\Omega^{(1)}) \text{ for (RSI)},$$
$$w_D \in H^1_0(\Omega^{(1)}) \text{ for (DSIH)}, \quad w_N \in H^1(\Omega^{(1)}) \text{ for (NSIH)},$$

such that for all $\varphi \in H^1(\Omega^{(1)})$, $\varphi_0 \in H^1_0(\Omega^{(1)})$, $\psi \in H^1(\Gamma)$,

$$\begin{aligned}
a_B(u,\varphi) + a_S(v,\psi) + Kl_S(v-\gamma_0(u),\psi-\gamma_0(\varphi)) &= l_B(f,\varphi) + \beta l_S(g,\psi),\\
a_S(v_S,\psi) &= l_S(g,\psi),\\
a_B(u_R,\varphi) + \beta l_S(\gamma_0(u_R),\gamma_0(\varphi)) &= l_B(f,\varphi) + \beta l_S(g,\gamma_0(\varphi)),\\
a_B(w_D,\varphi_0) &= l_B(f,\varphi_0) - a_B(\tilde{g},\varphi_0),\\
a_B(w_N,\varphi) &= l_B(f-\nabla\cdot(\mathcal{A}\nabla\hat{g}) - a\hat{g},\varphi).
\end{aligned}$$

We remark that one can consider (DSIH) as the limiting problem $\beta\to+\infty$ of the homogeneous Robin boundary condition:

$$\text{(RSIH)} \qquad \begin{aligned} -\nabla\cdot(\mathcal{A}\nabla w) + aw &= f - \nabla\cdot(\mathcal{A}\nabla\tilde{g}) - a\tilde{g} \text{ in } \Omega^{(1)},\\ \mathcal{A}\nabla w\cdot\nu + \beta w &= 0 \text{ on } \Gamma. \end{aligned}$$

In fact, we have

Lemma 5.10. *Let* $\Omega^{(1)}$ *be an open bounded domain with* C^1 *boundary* Γ*. Let the data satisfy Assumption 5.2 and suppose* $\tilde{g} \in H^1(\Omega^{(1)})$*. For each* $\beta > 0$*, let* $w^\beta \in H^1(\Omega^{(1)})$ *denote the unique weak solution to (RSIH). Then, as* $\beta\to\infty$*,* w^β *converges weakly to the unique weak solution to (DSIH) in* $H^1(\Omega^{(1)})$*.*

Proof. The weak formulation of (RSIH) is: Find $w \in H^1(\Omega^{(1)})$ such that for all $\varphi \in H^1(\Omega^{(1)})$,

$$\int_{\Omega^{(1)}} \mathcal{A}\nabla w \cdot \nabla\varphi + aw\varphi \, dx + \int_\Gamma \beta\gamma_0(w)\gamma_0(\varphi) \, d\mathcal{H} = \int_{\Omega^{(1)}} f\varphi - \mathcal{A}\nabla\tilde{g} \cdot \nabla\varphi - a\tilde{g}\varphi \, dx. \tag{5.2.11}$$

By the Lax–Milgram theorem, for each $\beta > 0$, there exists a unique weak solution $w^\beta \in H^1(\Omega^{(1)})$ to (RSIH). Moreover, w^β satisfies the following estimate:

$$\min(\theta_0, \theta_2) \left\| w^\beta \right\|^2_{H^1(\Omega^{(1)})} + 2\beta \left\| \gamma_0(w^\beta) \right\|^2_{L^2(\Gamma)} \leq \frac{\|f\|^2_{L^2(\Omega^{(1)})} + C_{\mathcal{A},a} \|\tilde{g}\|^2_{H^1(\Omega^{(1)})}}{\min(\theta_0, \theta_2)}.$$

From this, we observe that w^β is bounded in $H^1(\Omega^{(1)})$ uniformly in β. Hence there exists a subsequence $(\beta_i)_{i\in\mathbb{N}} \to \infty$ and a function $w^0 \in H^1(\Omega^{(1)})$ such that

$$w^{\beta_i} \to w^0 \in L^2(\Omega^{(1)}), \quad \nabla w^{\beta_i} \rightharpoonup \nabla w^0 \in L^2(\Omega^{(1)}) \text{ as } \beta_i \to \infty.$$

Compactness of the Boundary-Trace map (Theorem C.5) implies that $\gamma_0(w^\beta)$ converges strongly (and hence weakly) to $\gamma_0(w^0)$. By the lower semicontinuity of the norm with respect to the weak topology (Theorem C.14),

$$\left\| \gamma_0(w^0) \right\|_{L^2(\Gamma)} \leq \liminf_{\beta_i \to \infty} \left\| \gamma_0(w^{\beta_i}) \right\|_{L^2(\Gamma)} \leq \frac{C(\theta_0, \theta_1, f, \mathcal{A}, a, \tilde{g})}{\sqrt{\beta_i}} \to 0 \text{ as } \beta_i \to \infty.$$

Hence $\gamma_0(w^0) = 0$ almost everywhere on Γ. Since Γ is C^1, by the characterisation of zero trace Sobolev functions (Theorem C.4), we have $w^0 \in H^1_0(\Omega^{(1)})$. Testing with $\varphi \in H^1_0(\Omega^{(1)})$ in (5.2.11) and passing to the limit as $\beta \to \infty$, we see that w^0 satisfies

$$\int_{\Omega^{(1)}} \mathcal{A}\nabla w^0 \cdot \nabla\varphi + aw^0\varphi \, dx = \int_{\Omega^{(1)}} f\varphi - \mathcal{A}\nabla\tilde{g} \cdot \nabla\varphi - a\tilde{g}\varphi \, dx,$$

for all $\varphi \in H^1_0(\Omega^{(1)})$. Hence w^β converges (along a subsequence) to the solution of (DSIH) weakly in $H^1(\Omega^{(1)})$ as $\beta \to \infty$. Since (DSIH) is well-posed by the Lax–Milgram theorem, the aforementioned convergence applies to the whole sequence $\{w^\beta\}_\beta$, i.e., $w^\beta \to w_D$ almost everywhere in $\Omega^{(1)}$ as $\beta \to \infty$. □

Due to the presence of ξ_ε and δ_ε in the diffuse domain approximations, the natural function spaces to look for well-posedness are Sobolev spaces weighted by ξ_ε and δ_ε.

Definition 5.11. For fixed $\varepsilon > 0$, we define

$$L^2(\Omega_\varepsilon, \xi_\varepsilon) := \Big\{ f : \Omega_\varepsilon \to \mathbb{R} \text{ measurable s.t. } \int_{\Omega_\varepsilon} \xi_\varepsilon \, |f|^2 \, dx < \infty \Big\},$$
$$L^2(\Gamma_\varepsilon, \delta_\varepsilon) := \Big\{ f : \Gamma_\varepsilon \to \mathbb{R} \text{ measurable s.t. } \int_{\Gamma_\varepsilon} \delta_\varepsilon \, |f|^2 \, dx < \infty \Big\}.$$

By Theorem 1.5 of Kufner and Opic [1984], since $\xi_\varepsilon^{-1} \in L^1_{loc}(\Omega_\varepsilon)$, we have the continuous embedding $L^2(\Omega_\varepsilon, \xi_\varepsilon) \subset L^1_{loc}(\Omega_\varepsilon)$ by Hölder's inequality. Consequently, we can define derivatives for $f \in L^2(\Omega_\varepsilon, \xi_\varepsilon)$ in a distributional sense. I.e., for any multiindex α, we call a function g the α^{th} distributional derivative of f, and write $g = D^\alpha f$, if for every $\phi \in C_c^\infty(\Omega_\varepsilon)$,

$$\int_{\Omega_\varepsilon} f D^\alpha \phi \, dx = (-1)^{|\alpha|} \int_{\Omega_\varepsilon} g\phi \, dx.$$

We define

$$W^{1,2}(\Omega_\varepsilon, \xi_\varepsilon) := \left\{ f \in L^2(\Omega_\varepsilon, \xi_\varepsilon) : D^\alpha f \in L^2(\Omega_\varepsilon, \xi_\varepsilon) \text{ for } |\alpha| = 1 \right\}.$$

A similar definition $W^{1,2}(\Gamma_\varepsilon, \delta_\varepsilon)$ for Sobolev spaces weighted by δ_ε can be made since $\delta_\varepsilon^{-1} \in L^1_{loc}(\Gamma_\varepsilon)$.

We remark that for any $\varepsilon > 0$, $\xi_\varepsilon^{(1)}$ and $\delta_\varepsilon^{(1)}$ derived from the double-well potential are non-degenerate in Ω, i.e. $\Omega_\varepsilon = \Gamma_\varepsilon = \Omega$ for all $\varepsilon > 0$. However, $\xi_\varepsilon^{(2)}$ and $\delta_\varepsilon^{(2)}$ that originate from the double-obstacle potential are degenerate in Ω. In particular, for (5.2.10),

$$\Omega_\varepsilon = \Omega^{(1)} \cup \mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma), \quad \Gamma_\varepsilon = \mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma),$$
$$\Omega_{\varepsilon_1} \subset \Omega_{\varepsilon_2}, \quad \Gamma_{\varepsilon_1} \subset \Gamma_{\varepsilon_2} \quad \text{if } \varepsilon_1 < \varepsilon_2.$$

However, the framework of weighted Sobolev spaces is flexible enough to allow us to deduce well-posedness of the diffuse domain approximations with both the double-well and double-obstacle regularisations. For the convergence analysis in ε, we will present the proofs with the double-well regularisation in mind, and detail the necessary modifications for the double-obstacle regularisation afterwards.

To streamline the presentation, it is more convenient to have a fixed domain when working with weighted Sobolev spaces, hence we introduce the following notation:

Definition 5.12. For fixed $\varepsilon > 0$, we define

$$L^2(\Omega, \xi_\varepsilon) := \{f : \Omega \to \mathbb{R} \text{ measurable s.t. } f|_{\Omega_\varepsilon} \in L^2(\Omega_\varepsilon, \xi_\varepsilon)\},$$
$$H^1(\Omega, \xi_\varepsilon) := \{f : \Omega \to \mathbb{R} \text{ measurable s.t. } f|_{\Omega_\varepsilon} \in W^{1,2}(\Omega_\varepsilon, \xi_\varepsilon)\},$$

with inner products and induced norms:

$$\langle f, g\rangle_{L^2(\Omega,\xi_\varepsilon)} := \int_\Omega \xi_\varepsilon f g \, dx = \int_{\Omega_\varepsilon} \xi_\varepsilon f g \, dx, \quad \|f\|^2_{0,\xi_\varepsilon} = \langle f, f\rangle_{L^2(\Omega,\xi_\varepsilon)},$$
$$\langle f, g\rangle_{H^1(\Omega,\xi_\varepsilon)} := \int_\Omega \xi_\varepsilon (f g + \nabla f \cdot \nabla g) \, dx, \quad \|f\|^2_{1,\xi_\varepsilon} = \langle f, f\rangle_{H^1(\Omega,\varepsilon)}.$$

A similar notation is used for $L^2(\Omega, \delta_\varepsilon)$ and $H^1(\Omega, \delta_\varepsilon)$. Furthermore, we define

$$\mathcal{V}_\varepsilon := \{f : \Omega \to \mathbb{R} \text{ measurable s.t. } f|_{\Omega_\varepsilon} \in W^{1,2}(\Omega_\varepsilon, \xi_\varepsilon)\} \text{ with}$$
$$\langle f, g\rangle_{\mathcal{V}_\varepsilon} := \int_\Omega \xi_\varepsilon (f g + \nabla f \cdot \nabla g) + \delta_\varepsilon f g \, dx,$$

and

$$\mathcal{W}_\varepsilon := \{f : \Omega \to \mathbb{R} \text{ measurable s.t. } f|_{\Omega_\varepsilon} \in W^{1,2}(\Omega_\varepsilon, \xi_\varepsilon)\} \text{ with}$$
$$\langle f, g\rangle_{\mathcal{W}_\varepsilon} := \int_\Omega \xi_\varepsilon (f g + \nabla f \cdot \nabla g) + \frac{1}{\varepsilon}\delta_\varepsilon f g \, dx.$$

We observe that $H^1(\Omega, \xi_\varepsilon)$, $\mathcal{V}_\varepsilon$, and $\mathcal{W}_\varepsilon$ are the same vector space but with different inner products and induced norms. It will turn out that the well-posedness to (RDD), (DDDH) and (NDDH) depends critically on the choice of the inner product.

Similar to the above, we introduce

$$a^\varepsilon_B(\varphi, \psi) := \int_\Omega \xi_\varepsilon \mathcal{A}^E \nabla\varphi \cdot \nabla\psi + \xi_\varepsilon a^E \varphi\psi \, dx, \quad l^\varepsilon_B(\varphi, \psi) := \int_\Omega \xi_\varepsilon \varphi\psi \, dx,$$
$$a^\varepsilon_S(\varphi, \psi) := \int_\Omega \delta_\varepsilon \mathcal{B}^E \nabla\varphi \cdot \nabla\psi + \delta_\varepsilon b^E \varphi\psi \, dx, \quad l^\varepsilon_S(\varphi, \psi) := \int_\Omega \delta_\varepsilon \varphi\psi \, dx.$$

Theorem 5.13 (Well-posedness for the diffuse domain approximations)**.** *Suppose Assumptions 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, and 5.7 are satisfied. Then, for each $\varepsilon > 0$,*

there exist unique weak solutions

$$(u^\varepsilon, v^\varepsilon) \in \mathcal{V}_\varepsilon \times H^1(\Omega, \delta_\varepsilon) \text{ for (CDD)},$$
$$v_S^\varepsilon \in H^1(\Omega, \delta_\varepsilon) \text{ for (SDD)}, \quad u_R^\varepsilon \in \mathcal{V}_\varepsilon \text{ for (RDD)},$$
$$w_D^\varepsilon \in \mathcal{W}_\varepsilon \text{ for (DDDH)}, \quad w_N^\varepsilon \in H^1(\Omega, \xi_\varepsilon) \text{ for (NDDH)},$$

such that for all $\varphi \in H^1(\Omega, \xi_\varepsilon)$, $\psi \in H^1(\Omega, \delta_\varepsilon)$, $\phi \in \mathcal{V}_\varepsilon$, $\Phi \in \mathcal{W}_\varepsilon$,

$$a_B^\varepsilon(u^\varepsilon, \phi) + a_S^\varepsilon(v^\varepsilon, \psi) + K l_S^\varepsilon(v^\varepsilon - u^\varepsilon, \psi - \phi) = l_B^\varepsilon(f^E, \phi) + \beta l_S^\varepsilon(g^E, \psi), \tag{5.2.12}$$
$$a_S^\varepsilon(v_S^\varepsilon, \psi) = l_S^\varepsilon(g^E, \psi), \tag{5.2.13}$$
$$a_B^\varepsilon(u_R^\varepsilon, \phi) + \beta l_S^\varepsilon(u_R^\varepsilon, \phi) = l_B^\varepsilon(f^E, \phi) + \beta l_S^\varepsilon(g^E, \phi), \tag{5.2.14}$$
$$a_B^\varepsilon(w_D^\varepsilon + \tilde{g}^E, \Phi) + \frac{1}{\varepsilon} l_S^\varepsilon(w_D^\varepsilon, \Phi) = l_B^\varepsilon(f^E, \Phi), \tag{5.2.15}$$
$$a_B^\varepsilon(w_N^\varepsilon, \varphi) - l_B^\varepsilon(\nabla \cdot (\mathcal{A}^E \nabla \hat{g}^E) - a^E \hat{g}^E, \varphi) = l_B^\varepsilon(f^E, \varphi). \tag{5.2.16}$$

Moreover, the weak solutions satisfy

$$\|u^\varepsilon\|_{1,\xi_\varepsilon}^2 + \|u^\varepsilon\|_{0,\delta_\varepsilon}^2 + \|v^\varepsilon\|_{1,\delta_\varepsilon}^2 \le C(\left\|f^E\right\|_{L^2(\Omega)}^2 + \left\|g^E\right\|_{L^2(\Omega)}^2), \tag{5.2.17}$$
$$\|v_S^\varepsilon\|_{1,\delta_\varepsilon}^2 \le C \left\|g^E\right\|_{L^2(\Omega)}^2, \tag{5.2.18}$$
$$\|u_R^\varepsilon\|_{1,\xi_\varepsilon}^2 + \|u_R^\varepsilon\|_{0,\delta_\varepsilon}^2 \le C(\left\|f^E\right\|_{L^2(\Omega)}^2 + \left\|g^E\right\|_{L^2(\Omega)}^2), \tag{5.2.19}$$
$$\|w_D^\varepsilon\|_{1,\xi_\varepsilon}^2 + \|w_D^\varepsilon\|_{0,\frac{1}{\varepsilon}\delta_\varepsilon}^2 \le C(\left\|f^E\right\|_{L^2(\Omega)}^2 + \left\|\tilde{g}^E\right\|_{H^1(\Omega)}^2), \tag{5.2.20}$$
$$\|w_N^\varepsilon\|_{1,\xi_\varepsilon}^2 \le C(\left\|f^E\right\|_{L^2(\Omega)}^2 + \left\|\hat{g}^E\right\|_{H^2(\Omega)}^2), \tag{5.2.21}$$

where the constants C *are independent of* ε.

We note that, it is due to the fact that g^E is a constant extension of g in the normal direction that the estimates in (5.2.17), (5.2.18) and (5.2.19) are independent of ε.

We next state the convergence result:

Theorem 5.14 (Convergence of diffuse domain approximations)**.** *Suppose Assumptions 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, and 5.7 are satisfied. Then, as* $\varepsilon \to 0$,

$$\|u^\varepsilon - u\|_{H^1(\Omega^{(1)})} \to 0, \quad \left|\|v^\varepsilon\|_{1,\delta_\varepsilon} - \|v\|_{H^1(\Gamma)}\right| \to 0,$$
$$\left|\|v_S^\varepsilon\|_{1,\delta_\varepsilon} - \|v_S\|_{H^1(\Gamma)}\right| \to 0, \quad \|u_R^\varepsilon - u_R\|_{H^1(\Omega^{(1)})} \to 0,$$
$$\|w_N^\varepsilon - w_N\|_{H^1(\Omega^{(1)})} \to 0, \quad \|w_D^\varepsilon - w_D\|_{H^1(\Omega^{(1)})} \to 0.$$

5.3 Technical results

5.3.1 Change of variables in the tubular neighbourhood

Fix $\eta > 0$ so that there is a diffeomorphism between $\mathrm{Tub}^{\eta}(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. For $t \in (-\eta, \eta)$, let Γ_t denote the level set $\{x \in \Omega : d(x) = t\}$. Then, by the co-area formula (Theorem C.9), (5.2.2) and the fact that $|\nu| = 1$, we can write

$$\int_{\mathrm{Tub}^{\eta}(\Gamma)} f(x)\,|\nabla d(x)|\; dx = \int_{\mathrm{Tub}^{\eta}(\Gamma)} f(x)\; dx = \int_{-\eta}^{\eta}\int_{\Gamma_t} f\; d\mathcal{H}dt. \tag{5.3.1}$$

We define the map $\rho_t : \Gamma \to \Gamma_t$ by

$$\rho_t(p) = p + t\nu(p) \text{ for } p \in \Gamma. \tag{5.3.2}$$

This map is well-defined and is injective due to the diffeomorphism between $\mathrm{Tub}^{\eta}(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. Then, by a change of variables, we obtain

$$\int_{\Gamma_t} f\; d\mathcal{H} = \int_{\Gamma} f(p + t\nu(p))\left|\det((\nabla\rho_t)^T(\nabla\rho_t))\right|^{\frac{1}{2}} d\mathcal{H},$$

where $\nabla\rho_t$ is the Jacobian matrix of ρ_t. To identify $\det((\nabla\rho_t)^T\nabla\rho_t)$ as a function of t we use local coordinates.

Since Γ is a compact hypersurface, we can always find a finite open cover of Γ consisting of open sets $W_i \subset \mathbb{R}^n, 1 \le i \le N$ such that $\Gamma \subset \bigcup_{i=1}^{N} W_i$. For each $1 \le i \le N$, let $\alpha_i(s)$ denote a regular parameterisation of $W_i \cap \Gamma$ with parameter domain $\mathcal{S}_i \subset \mathbb{R}^{n-1}$, i.e., $\alpha_i : \mathcal{S}_i \to W_i \cap \Gamma$ is a local parameterisation of Γ. Let

$$J_{i,0}(s) := (\partial_{s_1}\alpha_i(s),\, \ldots,\, \partial_{s_{n-1}}\alpha_i(s),\, \nu(\alpha_i(s)) \in \mathbb{R}^{n\times n}.$$

Since α_i is a regular parameterisation, the tangent vectors $\{\partial_{s_j}\alpha\}_{1\le j\le n-1}$ are linearly independent and hence $\det J_{i,0} \neq 0$. Then for any $f \in L^1_{loc}(\Gamma)$,

$$\int_{W_i\cap\Gamma} f\; d\mathcal{H} = \int_{\mathcal{S}_i} f(\alpha_i(s))\,|\det J_{i,0}|\; ds. \tag{5.3.3}$$

By the injectivity of ρ_t, Γ_t is also a compact hypersurface with a finite open cover $\{\rho_t(W_i \cap \Gamma)\}_{i=1}^{N}$. In addition, $\rho_t \circ \alpha_i$ is a local parameterisation of Γ_t. Let

$$\begin{aligned} J_{i,\eta}(s,t) &:= (\partial_{s_1}\alpha_i(s) + t\partial_{s_1}\nu(\alpha_i(s)),\, \ldots,\, \partial_{s_{n-1}}\alpha_i(s) + t\partial_{s_{n-1}}\nu(\alpha_i(s)),\, \nu(\alpha_i(s))) \in \mathbb{R}^{n\times n} \\ &= J_{i,0}(s) + t(\partial_{s_1}\nu(\alpha_i(s)), \ldots,\, \partial_{s_{n-1}}\nu(\alpha_i(s)),\, 0) =: J_{i,0}(s) + tB_i(s). \end{aligned}$$

A short calculation shows that

$$\begin{aligned}\det J_{i,\eta} &= \det(J_{i,0}+tB_i) = (\det J_{i,0})(\det(I+tJ_{i,0}^{-1}B_i)) = (\det J_{i,0})t^n \det\left(t^{-1}I + J_{i,0}^{-1}B_i\right)\\ &= (\det J_{i,0}(s))t^n\left(\frac{1}{t^n} - \frac{1}{t^{n-1}}\mathrm{tr}\left(-J_{i,0}^{-1}B_i(s)\right) + \cdots + (-1)^n \det(-J_{i,0}^{-1}B_i(s))\right)\\ &= (\det J_{i,0}(s))\left(1 + \mathrm{tr}\left(tJ_{i,0}^{-1}B_i(s)\right) + \cdots + (-1)^{2n}\det(tJ_{i,0}^{-1}B_i(s))\right),\end{aligned}$$

where we have used the properties $\mathrm{tr}\,(cA) = c\mathrm{tr}\,(A)$ and $\det(cA) = c^n \det(A)$ for constant c and matrix A, and the well-known fact that the coefficients of the monic characteristic polynomial

$$\det(xI - A) = p_A(x) = x^n + a_{n-1}x^{n-1} + \ldots a_1 x + a_0,$$

are given by

$$a_{n-k} = (-1)^k \sum_{|\{i,j,\ldots,l\}|=k} \lambda_i\lambda_j\ldots\lambda_l, \quad k = 1,\ldots,n-1, \quad a_0 = (-1)^n\det(A),$$

where $\{\lambda_j\}_{j=1}^n$ are the eigenvalues of A (see Brooks [2006]). We define

$$C_{i,H}(s) := \mathrm{tr}\left(J_{i,0}^{-1}B_i(s)\right), \quad C_{i,R}(s,t)) := t^n p_{-J_{i,0}^{-1}B_i(s)}(1/t) - 1 - tC_{i,H}(s),$$

so that

$$\det J_{i,\eta}(s,t) = (\det J_{i,0}(s))(1 + tC_{i,H}(s) + C_{i,R}(s,t)).$$

For $n = 2$, if α is a global arclength parameterisation of Γ, then $N = 1$ and

$$|\det J_0(s)| = 1, \quad |\det J_\eta(s,t)| = |1 - \kappa(s)t|,$$

where κ is the curvature of Γ. This agrees with the calculation in Appendix B of Garcke and Stinner [2006]. Consequently, we have

$$\begin{aligned}\int_{\rho_t(W_i\cap\Gamma)} f\, d\mathcal{H} &= \int_{\mathcal{S}_i} f(\alpha_i(s) + t\nu(\alpha_i(s)))\,|\det J_{i,\eta}(s,t)|\; ds \qquad (5.3.4)\\ &= \int_{\mathcal{S}_i} f(\alpha_i(s) + t\nu(\alpha_i(s)))\,|\det J_{i,0}(s)|\,|1 + tC_{i,H}(s) + C_{i,R}(s,t)|\; ds.\end{aligned}$$

By Assumption 5.1, Γ is a C^3 hypersurface and so the eigenvalues of $J_{i,0}(s)$ and $J_{i,0}^{-1}B_i(s)$ are bounded uniformly in $s \in \mathcal{S}_i$. Hence, for each $1 \le i \le N$, there exists

a constant C_i such that

$$|\det J_{i,\eta}(s,t) - \det J_{i,0}(s)| \leq C_i t.$$

Let $\{\mu_i\}_{i=1}^N$ be a partition of unity subordinate to the covering $\{W_i \cap \Gamma\}_{i=1}^N$ of Γ. Consequently, by the diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$, we observe that $\{\mu_i\}_{i=1}^N$ is also a partition of unity subordinate to the covering $\{\rho_t(W_i \cap \Gamma)\}_{i=1}^N$ of Γ_t for $t \in (-\eta, \eta)$. Moreover, by the compactness of Γ, there are only a finite number of C_i and so we can deduce that there exists a constant $\tilde{c}$ (that can be chosen independent of η) such that, for all $t \in (-\eta, \eta), s \in \mathcal{S}_i, 1 \leq i \leq N$,

$$\max_{1 \leq i \leq N} |\det J_{i,\eta}(s,t) - \det J_{i,0}(s)| \leq \tilde{c} t.$$

We define

$$\mathcal{C}_H(p) := \sum_{i=1}^N \mu_i(\alpha_i(s)) \mathcal{C}_{i,H}(s), \quad \mathcal{C}_R(p,t) := \sum_{i=1}^N \mu_i(\alpha_i(s)) \mathcal{C}_{i,R}(s,t).$$

From the above discussion, we observe that $\mathcal{C}_H(p)$ and $\mathcal{C}_R(p,t)$ are bounded uniformly in $p \in \Gamma$ and

$$|t\mathcal{C}_H(p) + \mathcal{C}_R(p,t)| \leq \tilde{c}\,|t| \ \text{ for all } \ |t| < \eta. \tag{5.3.5}$$

Then, from (5.3.3), for any $f \in L^1(\Gamma)$,

$$\int_\Gamma f \, d\mathcal{H} = \sum_{i=1}^N \int_{W_i \cap \Gamma} \mu_i f \, d\mathcal{H} = \sum_{i=1}^N \int_{\mathcal{S}_i} (\mu_i f)(\alpha_i(s)) \, |\det J_{i,0}(s)| \, ds,$$

and similarly from (5.3.4), for any $f \in L^1(\mathrm{Tub}^\eta(\Gamma))$,

$$\begin{aligned}
&\int_{\mathrm{Tub}^\eta(\Gamma)} f(x) \, dx = \int_{-\eta}^{\eta} \int_{\Gamma_t} f \, d\mathcal{H} dt = \int_{-\eta}^{\eta} \sum_{i=1}^N \int_{\rho_t(W_i \cap \Gamma)} \mu_i f \, d\mathcal{H} dt \\
&= \int_{-\eta}^{\eta} \sum_{i=1}^N \int_{\mathcal{S}_i} (\mu_i f)(\alpha_i(s) + t\nu(\alpha_i(s))) \, |\det J_{i,0}(s)| \, |1 + t\mathcal{C}_{i,H}(s) + \mathcal{C}_{i,R}(s,t)| \, ds dt \\
&= \int_{-\eta}^{\eta} \sum_{i=1}^N \int_{W_i \cap \Gamma} f(p + t\nu(p)) \, |1 + t\mathcal{C}_H(p) + \mathcal{C}_R(p,t)| \, d\mathcal{H} dt \\
&= \int_{-\eta}^{\eta} \int_{\Gamma} f(p + t\nu(p)) \, |1 + t\mathcal{C}_H(p) + \mathcal{C}_R(p,t)| \, d\mathcal{H} dt.
\end{aligned} \tag{5.3.6}$$

Hence, we can identify $\left|\det((\nabla\rho_t)^T(\nabla\rho_t))\right|^{\frac{1}{2}}(p,t) = |1+t\mathcal{C}_H(p)+\mathcal{C}_R(p,t)|$. Furthermore, for η sufficiently small so that $\tilde{c}\eta < 1$, we have the following bounds:

$$\frac{1}{1+\tilde{c}\eta}\int_{\mathrm{Tub}^\eta(\Gamma)} f(x)\,dx \leq \int_{-\eta}^{\eta}\int_\Gamma f(p+t\nu(p))\,d\mathcal{H}dt \leq \frac{1}{1-\tilde{c}\eta}\int_{\mathrm{Tub}^\eta(\Gamma)} f(x)\,dx. \tag{5.3.7}$$

5.3.2 Coordinates in a scaled tubular neighbourhood

In the subsequent convergence analysis, we will use a tubular neighbourhood X^ε whose width scales with ε^k for some $0 < k \leq 1$, i.e., $X^\varepsilon = \mathrm{Tub}^{\varepsilon^k\eta}(\Gamma)$. For this section, we take $X^\varepsilon = \mathrm{Tub}^{\varepsilon\eta}(\Gamma)$ to derive some technical results.

We introduce the rescaled distance variable

$$z := \frac{d}{\varepsilon}.$$

Let $p(x)$ denote the closest point operator of x as defined in (5.2.1). Then, for any $x \in X^\varepsilon$, we have

$$x = p(x) + \varepsilon z\nu(p(x)), \tag{5.3.8}$$

for some $z \in (-\eta,\eta)$. With a regular local parameterisation of Γ, $\alpha : \mathcal{S} \subset \mathbb{R}^{n-1} \to W \cap \Gamma$, $W \subset \mathbb{R}^n$ open set, we can define

$$G_\varepsilon(s,z) = \alpha(s) + \varepsilon z\nu(\alpha(s)). \tag{5.3.9}$$

For any scalar function $f(x)$, we define its representation $F_\varepsilon(s,z)$ in the (s,z) coordinate system by

$$F_\varepsilon(s,z) := f(\alpha(s)+\varepsilon z\nu(\alpha(s))) \text{ for some } s \in \mathcal{S}, z \in (-\eta,\eta).$$

For $z \in (-\eta,\eta)$, we define a parallel hypersurface at distance εz away from Γ as

$$\Gamma^{\varepsilon z} := \{p + \varepsilon z\nu(p) : p \in \Gamma\}.$$

Then by the injectivity of the closest point operator, we have

$$\nu(y) = \nu(p(y)) \text{ for } y \in \Gamma^{\varepsilon z}. \tag{5.3.10}$$

Moreover, we have the following:

Lemma 5.15. *Let $f : X^\varepsilon \to \mathbb{R}$ be a C^1 function with representation F_ε in the (s, z) coordinate system. Then*

$$\nabla f(x) = \nabla_{\Gamma^{\varepsilon z}} F_\varepsilon(s, z) + \frac{1}{\varepsilon}\nu(\alpha(s))\partial_z F_\varepsilon(s, z), \tag{5.3.11}$$

where $\nabla_{\Gamma^{\varepsilon z}}(\cdot)$ denotes the surface gradient on $\Gamma^{\varepsilon z}$. In addition, for $x = \alpha(s) + \varepsilon z\nu(\alpha(s)) \in X^\varepsilon$,

$$\nabla_{\Gamma^{\varepsilon z}} F_\varepsilon(s, z) = \nabla_\Gamma F_\varepsilon(s, z) + \mathcal{O}(\varepsilon z) \text{ as } \varepsilon \to 0. \tag{5.3.12}$$

Proof. We follow the proof given in the appendix of Abels et al. [2011]. The equivalent result in two dimensions can be found in Elliott and Stinner [2009] and Appendix B of Garcke and Stinner [2006]. Let $(s_1, \dots, s_{n-1}) \in \mathcal{S}$, $s_n := z$, then by (5.3.9),

$$\partial_{s_i} G_\varepsilon = \partial_{s_i}\alpha + \varepsilon z\partial_{s_i}\nu \text{ for } 1 \le i \le n-1, \quad \partial_{s_n} G_\varepsilon = \varepsilon\nu,$$

and $\{\partial_{s_i} G_\varepsilon\}_{i=1}^n$ is a basis of $\mathbb{R}^n$ locally around Γ. For $1 \le i, j \le n-1$, we define the metric tensor in the new coordinates as

$$\begin{aligned} g_{ij} &= (\partial_{s_i}\alpha + \varepsilon z\partial_{s_i}\nu) \cdot (\partial_{s_j}\alpha + \varepsilon z\partial_{s_j}\nu), \\ g_{in} = g_{ni} &= (\partial_{s_i}\alpha + \varepsilon z\partial_{s_i}\nu) \cdot \varepsilon\nu = 0, \quad g_{nn} = \varepsilon\nu \cdot \varepsilon\nu = \varepsilon^2, \end{aligned}$$

where we have used that $\partial_{s_i}\nu \cdot \nu = \frac{1}{2}\partial_{s_i} |\nu|^2 = 0$. Setting

$$\mathcal{G}_{\varepsilon z} = (g_{ij})_{1\le i,j\le n}, \quad \widetilde{\mathcal{G}}_{\varepsilon z} = (g_{ij})_{1\le i,j\le n-1},$$

with corresponding inverses

$$\mathcal{G}_{\varepsilon z}^{-1} = (g^{ij})_{1\le i,j\le n}, \quad \widetilde{\mathcal{G}}_{\varepsilon z}^{-1} = (g^{ij})_{1\le i,j\le n-1}.$$

Then

$$\mathcal{G}_{\varepsilon z} = \begin{pmatrix} & & 0 \\ & \widetilde{\mathcal{G}}_{\varepsilon z} & \vdots \\ & & 0 \\ 0 \dots 0 & & \varepsilon^2 \end{pmatrix}, \quad \mathcal{G}_{\varepsilon z}^{-1} = \begin{pmatrix} & & 0 \\ & \widetilde{\mathcal{G}}_{\varepsilon z}^{-1} & \vdots \\ & & 0 \\ 0 \dots 0 & & \varepsilon^{-2} \end{pmatrix}.$$

For any scalar function $f(x) = F_\varepsilon(s(x), z(x))$, we have

$$\begin{aligned}\nabla f(x) &= \sum_{j=1}^{n} \left(\sum_{i=1}^{n} g^{ij} \partial_{s_i} F_\varepsilon \right) \partial_{s_j} G_\varepsilon \\ &= \sum_{j=1}^{n-1} \left(\sum_{i=1}^{n-1} g^{ij} \partial_{s_i} F_\varepsilon \right) \partial_{s_j} G_\varepsilon + \frac{1}{\varepsilon^2} \partial_z F_\varepsilon \partial_z G_\varepsilon = \nabla_{\Gamma^{\varepsilon z}} F_\varepsilon + \frac{1}{\varepsilon} \partial_z F_\varepsilon \nu.\end{aligned}$$

This shows the first assertion.

Let A, B and C denote the matrices with the following entries: For $1 \leq i, j \leq n-1$,

$$A_{ij} := \partial_{s_i} \alpha \cdot \partial_{s_j} \alpha, \quad B_{ij} := \partial_{s_i} \nu \cdot \partial_{s_j} \alpha + \partial_{s_i} \alpha \cdot \partial_{s_j} \nu, \quad C_{ij} := \partial_{s_i} \nu \cdot \partial_{s_j} \nu.$$

Then, a calculation involving the ansatz,

$$\tilde{\mathcal{G}}_{\varepsilon z}^{-1} = (A + \varepsilon z B + \varepsilon^2 z^2 C)^{-1} = A^{-1} + D,$$

will yield that

$$D = -(I + A^{-1}(\varepsilon z B + \varepsilon^2 z^2 C))^{-1} (A^{-1}(\varepsilon z B + \varepsilon^2 z^2 C) A^{-1}),$$

if $\tilde{\mathcal{G}}_{\varepsilon z}$, A and $I + A^{-1}(\varepsilon z B + \varepsilon^2 z^2 C)$ are invertible. Hence

$$\tilde{\mathcal{G}}_{\varepsilon z}^{-1} = A^{-1} - (I + A^{-1}(\varepsilon z B + \varepsilon^2 z^2 C))^{-1} (A^{-1}(\varepsilon z B + \varepsilon^2 z^2 C) A^{-1}).$$

Since Γ is a C^3 hypersurface, all entries in the matrices A, B, and C are bounded. For a matrix H and ε sufficiently small so that the absolute value of the eigenvalues of εH are less than 1, we have,

$$(I + \varepsilon H)^{-1} = I - \varepsilon H + \varepsilon^2 H^2 - \dots.$$

Hence, we can express

$$\tilde{\mathcal{G}}_{\varepsilon z}^{-1} = A^{-1} - \varepsilon z A^{-1} B A^{-1} + \mathcal{O}(\varepsilon^2) \text{ as } \varepsilon \to 0.$$

In particular,

$$\nabla_{\Gamma^{\varepsilon z}} F_\varepsilon(s,z) = \sum_{i,j=1}^{n-1} g^{ij} \partial_{s_i} F_\varepsilon \partial_{s_j} G_\varepsilon$$

$$= \sum_{i,j=1}^{n-1} A^{ij} \partial_{s_i} F_\varepsilon \partial_{s_j} \alpha + \varepsilon z \sum_{i,j=1}^{n-1} \left(A^{ij} \partial_{s_i} F_\varepsilon \partial_{s_j} \nu(\alpha) - (A^{-1} B A^{-1})_{ij} \partial_{s_i} F_\varepsilon \partial_{s_j} \alpha \right) + \text{ h.o.t.}$$

$$= \nabla_\Gamma F_\varepsilon(s,z) + \mathcal{O}(\varepsilon z) \text{ as } \varepsilon \to 0.$$

□

We remark that in two-dimensions, for an arclength parameterisation $\alpha : \mathcal{S} \subset \mathbb{R} \to \Gamma$ of Γ, we have that $A = 1$, $\partial_s \nu = -\kappa \partial_s \alpha$, $B = -2\varepsilon z \kappa$ and $\nabla_\Gamma F(s,z) = \partial_s F_\varepsilon(s,z) \partial_s \alpha(s)$. Hence, we obtain from (5.3.11) and (5.3.12),

$$\nabla f = \frac{1}{\varepsilon} \partial_z F_\varepsilon \nu + \partial_s F_\varepsilon \partial_s \alpha + \varepsilon z \kappa \partial_s F_\varepsilon \partial_s \alpha + \mathcal{O}(\varepsilon^2),$$

which is consistent with Appendix B of Garcke and Stinner [2006].

Locally, we define $\nabla^\Gamma_{\varepsilon z} F_\varepsilon$ to be

$$\nabla^\Gamma_{\varepsilon z} F_\varepsilon(s,z) := \nabla_{\Gamma^{\varepsilon z}} F_\varepsilon(s,z) - \nabla_\Gamma F_\varepsilon(s,z), \tag{5.3.13}$$

and we note that by definition, $\nabla^\Gamma_{\varepsilon z} F_\varepsilon(s,z) \cdot \nu(\alpha(s)) = 0$ for all $s \in \mathcal{S}_i$, $1 \le i \le N$.

Using (5.3.8) we can define the representation of a function $f(x)$ in the global (p,z) coordinate system, $F_\varepsilon(p,z)$, by

$$F_\varepsilon(p,z) := f(p + \varepsilon z \nu(p)), \tag{5.3.14}$$

for $p \in \Gamma$ such that $x = p + \varepsilon z \nu(p)$, $z \in (-\eta, \eta)$. Then the conclusions of Lemma 5.15 can be translated to: For any $f \in C^1(X^\varepsilon)$ and its representation $F_\varepsilon(p,z)$ in the (p,z) coordinate system,

$$\nabla f(x) = \frac{1}{\varepsilon} \nu(p) \partial_z F_\varepsilon(p,z) + \nabla_\Gamma F_\varepsilon(p,z) + \nabla^\Gamma_{\varepsilon z} F_\varepsilon(p,z), \tag{5.3.15}$$

where

$$\nabla^\Gamma_{\varepsilon z} F_\varepsilon(p,z) \sim \mathcal{O}(\varepsilon z) \text{ as } \varepsilon \to 0.$$

Moreover, by the co-area formula, (5.3.6), (5.3.15), and that $\nabla_{\Gamma^{\varepsilon z}} F_\varepsilon \cdot \nu = 0$, we have

$$\begin{aligned}
&\int_{\mathrm{Tub}^{\varepsilon\eta}(\Gamma)} |f(x)|^2 + |\nabla f(x)|^2 \ dx = \int_{-\varepsilon\eta}^{\varepsilon\eta} \int_{\Gamma_t} |f|^2 + |\nabla f|^2 \ d\mathcal{H} dt \\
&= \int_{-\eta}^{\eta} \int_{\Gamma} \varepsilon(|f|^2 + |\nabla f|^2)(p + \varepsilon z \nu(p)) \, |1 + \varepsilon z \mathcal{C}_H(p) + \mathcal{C}_R(p, \varepsilon z)| \ d\mathcal{H}(p) dz \quad (5.3.16) \\
&= \int_{-\eta}^{\eta} \int_{\Gamma} \frac{1}{\varepsilon} |\partial_z F_\varepsilon|^2 (p, z) \, |1 + \varepsilon z \mathcal{C}_H(p) + \mathcal{C}_R(p, \varepsilon z)| \ d\mathcal{H}(p) dz \\
&+ \int_{-\eta}^{\eta} \int_{\Gamma} \varepsilon \left(|F_\varepsilon|^2 + \left| \nabla_\Gamma F_\varepsilon + \nabla^\Gamma_{\varepsilon z} F_\varepsilon \right|^2 \right) (p, z) \, |1 + \varepsilon z \mathcal{C}_H(p) + \mathcal{C}_R(p, \varepsilon z)| \ d\mathcal{H}(p) dz.
\end{aligned}$$

We remark that for any intermediate scaling, $\mathrm{Tub}^{\varepsilon^k \eta}(\Gamma)$ for $0 < k < 1$, the above calculation gives

$$\begin{aligned}
&\int_{\mathrm{Tub}^{\varepsilon^k \eta}(\Gamma)} |f(x)|^2 + |\nabla f(x)|^2 \ dx \\
&= \int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_{\Gamma} \frac{1}{\varepsilon} |\partial_z F_\varepsilon|^2 (p, z) \, |1 + \varepsilon z \mathcal{C}_H(p) + \mathcal{C}_R(p, \varepsilon z)| \ d\mathcal{H}(p) dz \quad (5.3.17) \\
&+ \int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_{\Gamma} \varepsilon \left(|F_\varepsilon|^2 + \left| \nabla_\Gamma F_\varepsilon + \nabla^\Gamma_{\varepsilon z} F_\varepsilon \right|^2 \right) (p, z) \, |1 + \varepsilon z \mathcal{C}_H(p) + \mathcal{C}_R(p, \varepsilon z)| \ d\mathcal{H}(p) dz.
\end{aligned}$$

5.3.3 On functions extended constantly along the normal direction

Let $f \in H^1(\Gamma)$ and f^e denote its constant extension off Γ, as defined in (5.2.3). We can relate ∇f^e and $\nabla_\Gamma f$ by the following lemma:

Lemma 5.16. *Let $\boldsymbol{H}$ denote the Hessian of the signed distance function d, then*

$$\nabla f^e(x) = (I - d(x)\boldsymbol{H}(x)) \nabla_\Gamma f(p(x)), \quad (5.3.18)$$

where I is the identity tensor. Consequently,

$$\nabla f^e(x) = \nabla_\Gamma f(x) \text{ for } x \in \Gamma. \quad (5.3.19)$$

Proof. Let $P := I - \nu \otimes \nu$ denote the projection operator to the tangent space. Then a direct calculation shows that

$$P\boldsymbol{H} = \boldsymbol{H}P = \boldsymbol{H}.$$

Define f^e as in (5.2.3) and using the Chain rule we obtain

$$\nabla f^e(x) = \nabla p(x) \nabla f(p(x)) = (I - \nabla d \otimes \nu - d\boldsymbol{H})(x) \nabla f(p(x)).$$

Since d is the signed distance function, we have $\nabla d(x) = \nu(p(x))$ for $x \in \mathrm{Tub}^\eta(\Gamma)$. Hence, for $x \in \mathrm{Tub}^\eta(\Gamma)$, we have

$$\begin{aligned}\nabla f^e(x) &= (P - d(x)\boldsymbol{H}(x)) \nabla f(p(x)) \\ &= (I - d(x)\boldsymbol{H}(x)) P \nabla f(p(x)) = (I - d(x)\boldsymbol{H}(x)) \nabla_\Gamma f(p(x)).\end{aligned}$$

□

Corollary 5.17. *Let $f \in H^1(\Gamma)$. Then there exists $f^E \in H^1(\Omega)$ such that*

$$\gamma_0(f^E) \equiv f \text{ on } \Gamma,$$

and there exists a constant $C > 0$, independent of f, such that

$$\left\|f^E\right\|_{L^2(\Omega)} \leq C \left\|f\right\|_{L^2(\Gamma)}, \quad \left\|\nabla f^E\right\|_{L^2(\Omega)} \leq C \left\|\nabla_\Gamma f\right\|_{L^2(\Gamma)}.$$

Proof. Fix η so that there is a diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. By Assumption 5.1, Γ is a C^3 hypersurface and so

$$\|\boldsymbol{H}\|_{C^0(\mathrm{Tub}^\eta(\Gamma))} \leq \|d\|_{C^2(\mathrm{Tub}^\eta(\Gamma))} < \infty. \tag{5.3.20}$$

Let $f \in H^1(\Gamma)$ and define f^e as the extension of f as in (5.2.3) to $\mathrm{Tub}^\eta(\Gamma)$. Then by (5.3.5), and (5.3.6),

$$\begin{aligned}\int_{\mathrm{Tub}^\eta(\Gamma)} |f^e(x)|^2 \, dx &= \int_{\mathrm{Tub}^\eta(\Gamma)} |f(p(x))|^2 \, dx \\ &= \int_{-\eta}^{\eta} \int_\Gamma |f(p)|^2 \, |1 + t\mathcal{C}_H(p) + \mathcal{C}_R(p,t)| \, d\mathcal{H} dt \leq C(\tilde{c}\eta) \left\|f\right\|^2_{L^2(\Gamma)},\end{aligned}$$

and

$$\begin{aligned}\int_{\mathrm{Tub}^\eta(\Gamma)} |\nabla f^e(x)|^2 \, dx &= \int_{\mathrm{Tub}^\eta(\Gamma)} |\nabla_\Gamma f - d(x)\boldsymbol{H}(x)\nabla_\Gamma f(p(x))|^2 \, dx \\ &\leq (1 + \|d\|_{C^0(\mathrm{Tub}^\eta(\Gamma))} \|\boldsymbol{H}\|_{C^0(\mathrm{Tub}^\eta(\Gamma))}) \int_{\mathrm{Tub}^\eta(\Gamma)} |\nabla_\Gamma f|^2 (p(x)) \, dx \\ &\leq (1 + \|d\|_{C^2(\mathrm{Tub}^\eta(\Gamma))}) C(\tilde{c}\eta) \left\|\nabla_\Gamma f\right\|^2_{L^2(\Gamma)}.\end{aligned}$$

Hence,

$$\int_{\mathrm{Tub}^\eta(\Gamma)} |f^e(x)|^2 + |\nabla f^e(x)|^2 \ dx \leq C(\tilde{c}\eta, \|d\|_{C^2(\mathrm{Tub}^\eta(\Gamma))}) \|f\|^2_{H^1(\Gamma)},$$

and so $f^e \in H^1(\mathrm{Tub}^\eta(\Gamma))$. We now use the Extension theorem (Theorem C.2) to extend f^e to a function $f^E \in H^1(\Omega)$ such that

$$\left\|f^E\right\|_{H^1(\Omega)} \leq C \|f^e\|_{H^1(\mathrm{Tub}^\eta(\Gamma))} \leq C \|f\|_{H^1(\Gamma)}.$$

□

The next lemma allows us to test with extensions of $H^1(\Gamma)$ functions in the weak formulations of the diffuse domain approximations.

Lemma 5.18. *Let $f \in H^1(\Gamma)$ and let f^E denote its extension to Ω constructed in the proof of Corollary 5.17. Then for all $\varepsilon > 0$,*

$$f^E \in H^1(\Omega, \delta_\varepsilon),$$

and there exists a constant $C > 0$, independent of f and ε, such that

$$\left\|f^E\right\|_{0,\delta_\varepsilon} \leq C \|f\|_{L^2(\Gamma)}, \quad \left\|\nabla f^E\right\|_{0,\delta_\varepsilon} \leq C \|\nabla_\Gamma f\|_{L^2(\Gamma)},$$

and

$$\int_\Omega \delta_\varepsilon \left|f^E\right|^2 \ dx \to \int_\Gamma |f|^2 \ d\mathcal{H}, \quad \int_\Omega \delta_\varepsilon \left|\nabla f^E\right|^2 \ dx \to \int_\Gamma |\nabla_\Gamma f|^2 \ d\mathcal{H}, \tag{5.3.21}$$

as $\varepsilon \to 0$.

Proof. Fix $\eta > 0$ so that there is a diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. As a consequence of (5.2.6), we have for $q_1 = q_2 = 1$,

$$\|\delta_\varepsilon(x)\|_{L^\infty(\Omega \setminus \mathrm{Tub}^\eta(\Gamma))} \to 0 \text{ as } \varepsilon \to 0, \tag{5.3.22}$$

and so, for $\varepsilon \in (0, 1]$,

$$\|\delta_\varepsilon(x)\|_{L^\infty(\Omega \setminus \mathrm{Tub}^\eta(\Gamma))} \leq \sup_{\varepsilon \in (0,1]} \|\delta_\varepsilon(x)\|_{L^\infty(\Omega \setminus \mathrm{Tub}^\eta(\Gamma))} =: C_{\sup}. \tag{5.3.23}$$

By (5.3.5), (5.3.6), (5.2.3), (5.2.5), a change of variable $t := \varepsilon \tilde{t}$, and Corollary

5.17, we see that

$$\begin{aligned}
&\int_\Omega \delta_\varepsilon \left|f^E\right|^2 \, dx \leq \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon \left|f^e\right|^2 \, dx + \|\delta_\varepsilon\|_{L^\infty(\Omega\setminus\mathrm{Tub}^\eta(\Gamma))} \left\|f^E\right\|^2_{L^2(\Omega\setminus\mathrm{Tub}^\eta(\Gamma))} \\
&\leq \int_{\frac{-\eta}{\varepsilon}}^{\frac{\eta}{\varepsilon}} \int_\Gamma \delta(\tilde{t}) \left|f^e\right|^2 (p+\varepsilon\tilde{t}\nu(p)) \left|1+\varepsilon\tilde{t}C_H(p)+C_R(p,\varepsilon\tilde{t})\right| \, d\mathcal{H}d\tilde{t} + C_{\sup} \left\|f^E\right\|^2_{L^2(\Omega)} \\
&\leq (1+\tilde{c}\eta) \|f\|^2_{L^2(\Gamma)} + C_{\sup} \left\|f^E\right\|^2_{L^2(\Omega)} \leq C \|f\|^2_{L^2(\Gamma)},
\end{aligned}$$

and so, $f^E \in L^2(\Omega, \delta_\varepsilon)$. Furthermore,

$$\begin{aligned}
&\left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon \left|f^e\right|^2 \, dx - \int_\Gamma |f|^2 \, d\mathcal{H} \right| \\
&= \left| \int_{\frac{-\eta}{\varepsilon}}^{\frac{\eta}{\varepsilon}} \int_\Gamma \delta(\tilde{t}) \left|f\right|^2 (p) \left|1+\varepsilon\tilde{t}\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon\tilde{t})\right| \, d\mathcal{H}d\tilde{t} - \int_{\mathbb{R}} \int_\Gamma \delta(\tilde{t}) \left|f\right|^2 \, d\mathcal{H}d\tilde{t} \right| \\
&\leq \left| \int_{\mathbb{R}} \chi_{\mathbb{R}\setminus(\frac{-\eta}{\varepsilon},\frac{\eta}{\varepsilon})}(\tilde{t})\delta(\tilde{t}) \, d\tilde{t} \right| \|f\|^2_{L^2(\Gamma)} + \varepsilon\tilde{c}C_{\delta,\mathrm{int}} \|f\|^2_{L^2(\Gamma)} \to 0 \text{ as } \varepsilon \to 0,
\end{aligned}$$

and so by (5.3.22),

$$\begin{aligned}
\left| \int_\Omega \delta_\varepsilon \left|f^E\right|^2 \, dx - \int_\Gamma |f|^2 \, d\mathcal{H} \right| \leq{}& \left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon \left|f^e\right|^2 \, dx - \int_\Gamma |f|^2 \, d\mathcal{H} \right| \\
&+ \|\delta_\varepsilon\|_{L^\infty(\Omega\setminus\mathrm{Tub}^\eta(\Gamma))} \left\|f^E\right\|^2_{L^2(\Omega\setminus\mathrm{Tub}^\eta(\Gamma))} \to 0 \text{ as } \varepsilon \to 0.
\end{aligned}$$

The assertion regarding the gradients follows via a similar argument with (5.3.20) and hence we omit the details. □

For the double-obstacle regularisation, we use the tubular neighbourhood $\mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma)$ and use the fact that $\delta_\varepsilon \equiv 0$ on $\Omega \setminus \mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma)$ to deduce the same results.

5.3.4 On the regularised indicator functions

As a consequence of (5.2.4) and Lebesgue dominated convergence theorem (Theorem C.1), we have

Lemma 5.19. *Assume that ξ_ε satisfies Assumption 5.6, then for any $g \in L^p(\Omega)$, $1 \leq p < \infty$,*

$$\int_{\Omega^{(1)}} \xi_\varepsilon |g|^p \, dx \to \int_{\Omega^{(1)}} |g|_{\Omega^{(1)}}|^p \, dx, \quad \int_{\Omega\setminus\Omega^{(1)}} \xi_\varepsilon |g|^p \, dx \to 0 \text{ as } \varepsilon \to 0.$$

Lemma 5.20. *Assume that ξ_ε satisfies Assumption 5.6 for $\varepsilon \in (0,1]$. Let $u^\varepsilon \in H^1(\Omega, \xi_\varepsilon)$ and suppose there exists a constant C, independent of ε, such that*

$$\|u^\varepsilon\|_{1,\xi_\varepsilon} \leq C.$$

Then there exists $\tilde{u} \in H^1(\Omega^{(1)})$ such that

$$u^\varepsilon|_{\Omega^{(1)}} \rightharpoonup \tilde{u} \text{ in } H^1(\Omega^{(1)}) \text{ as } \varepsilon \to 0,$$

along a subsequence.

Proof. By Assumption 5.6, $\xi_\varepsilon \geq \frac{1}{2}$ for $x \in \overline{\Omega^{(1)}}$, and so,

$$\|u^\varepsilon|_{\Omega^{(1)}}\|_{H^1(\Omega^{(1)})} \leq 2\int_{\Omega^{(1)}} \xi_\varepsilon |u^\varepsilon|^2 \, dx \leq 2\int_\Omega \xi_\varepsilon |u^\varepsilon|^2 \, dx \leq 2C \text{ for all } \varepsilon \in (0,1].$$

The assertion follows from reflexive weak compactness theorem (Theorem C.11). □

Lemma 5.21. *Assume that δ_ε satisfies Assumption 5.7 for $\varepsilon \in (0,1]$. Then, for any $f \in H^1(\Omega)$, there exists a constant $C > 0$, independent of f and ε, such that*

$$\|f\|_{0,\delta_\varepsilon} \leq C \|f\|_{H^1(\Omega)}.$$

Proof. Fix $\eta > 0$ so that there is a diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. Then, by (5.3.23),

$$\begin{aligned}
\int_\Omega \delta_\varepsilon |f|^2 \, dx &= \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon |f|^2 \, dx + \int_{\Omega \setminus \mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon |f|^2 \, dx \\
&\leq \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon |f|^2 \, dx + C_{\sup} \|f\|^2_{L^2(\Omega \setminus \mathrm{Tub}^\eta(\Gamma))} \\
&\leq \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon |f|^2 \, dx + C_{\sup} \|f\|^2_{H^1(\Omega)}.
\end{aligned}$$

By the diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$, we have $f^2|_{\mathrm{Tub}^\eta(\Gamma)} \in W^{1,1}((\Gamma \times (-\eta, \eta))$. By absolute continuity on lines for $W^{1,1}$ functions (Theorem C.10) there exists a version of f^2 (denoted again by the same symbol) such that for a.e. $p \in \Gamma$, it is absolutely continuous as a function of $t \in (-\eta, \eta)$. With absolute continuity with respect to t, we have

$$(f^2)(p + t\nu(p)) = (f^2)(p,t) = (f^2)(p,0) + \int_0^t \frac{d}{d\zeta}(f^2)(p,\zeta) \, d\zeta \text{ for } t \in (-\eta, \eta).$$

Then, by (5.2.5), (5.3.5), (5.3.6), (5.3.7) and a change of variables $t = \varepsilon\tilde{t}$,

$$\begin{aligned}
&\int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon |f|^2 \, dx = \int_{-\eta}^{\eta} \int_\Gamma \frac{1}{\varepsilon}\delta\left(\frac{t}{\varepsilon}\right) |f|^2 (p + t\nu(p)) \, |1 + t\mathcal{C}_H(p) + \mathcal{C}_R(p,t)| \, d\mathcal{H}dt \\
&= \int_{-\eta}^{\eta} \int_\Gamma \frac{1}{\varepsilon}\delta\left(\frac{t}{\varepsilon}\right) \left[|f|^2 (p) + \int_0^t \frac{d}{d\zeta} |f|^2 (p,\zeta) \, d\zeta \right] |1 + t\mathcal{C}_H(p) + \mathcal{C}_R(p,t)| \, d\mathcal{H}dt \\
&\leq \left(\left\| \gamma_0(|f|^2) \right\|_{L^1(\Gamma)} + \int_\Gamma \int_{-\eta}^{\eta} \left| \frac{d}{d\zeta} |f|^2 \right| \, d\zeta d\mathcal{H} \right) \int_{\frac{-\eta}{\varepsilon}}^{\frac{\eta}{\varepsilon}} \delta(\tilde{t})(1 + \varepsilon\tilde{c}\,|\tilde{t}|) \, d\tilde{t} \\
&\leq (1 + \varepsilon\tilde{c}C_{\delta,\mathrm{int}}) \Big(\left\| \gamma_0(|f|^2) \right\|_{L^1(\Gamma)} + C(\tilde{c}\eta) \left\| \nabla(|f|^2) \right\|_{L^1(\mathrm{Tub}^\eta(\Gamma))} \Big) \\
&\leq (1 + \tilde{c}C_{\delta,\mathrm{int}}) \Big(\left\| \gamma_0(|f|^2) \right\|_{L^1(\Gamma)} + C(\tilde{c}\eta) \, \|f\|^2_{H^1(\mathrm{Tub}^\eta(\Gamma))} \Big).
\end{aligned}$$

Then, by the Boundary-Trace theorem, we obtain

$$\int_\Omega \delta_\varepsilon |f|^2 \, dx \leq \big((1 + \tilde{c}C_{\delta,\mathrm{int}})(C_{\mathrm{tr}}^2 + C(\tilde{c}\eta)) + C_{\sup} \big) \, \|f\|^2_{H^1(\Omega)} \,,$$

where C_{tr} is the constant from the Boundary-Trace theorem. □

For the double-obstacle regularisation, we can neglect the contribution from the integral over $\Omega \setminus \mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma)$ and directly obtain

$$\|f\|^2_{0,\delta_\varepsilon} = \int_{\mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma)} \delta_\varepsilon |f|^2 \, dx \leq (1 + \tilde{c}C_{\delta,\mathrm{int}})(C_{\mathrm{tr}}^2 + C(\tilde{c}\eta)) \, \|f\|^2_{H^1(\Omega)} \,.$$

Lemma 5.22. *Suppose that Assumptions 5.1 and 5.7 are satisfied. For $f \in W^{1,1}(\Omega)$, we have*

$$\int_\Omega \delta_\varepsilon f \, dx \to \int_\Gamma \gamma_0(f) \, d\mathcal{H} \text{ as } \varepsilon \to 0. \tag{5.3.24}$$

Moreover, for $\eta > 0$ sufficiently small, if $f \in W^{1,q}(\Omega)$, $1 \leq q < \infty$ or $f \in C^1(\overline{\Omega})$ and $q = \infty$, then there exists a constant $C > 0$, independent of f and ε, such that

$$\left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f) \, d\mathcal{H} \right| \leq C\varepsilon^{1-\frac{1}{q}} \, \|f\|_{W^{1,q}(\Omega)} \,. \tag{5.3.25}$$

Furthermore, for any $f \in W^{1,q}(\Omega)$, $2 \leq q < \infty$ with $\gamma_0(f) = 0$, we have

$$\int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon |f|^2 \, dx \leq C\varepsilon^{2-\frac{2}{q}} \, \|f\|^2_{W^{1,q}(\Omega)} \,, \tag{5.3.26}$$

where C is independent of f and ε.

Proof. We note that the integrals are well-defined by the Boundary-Trace theorem and Lemma 5.21. Let $f \in C^1(\overline{\Omega})$, then $\gamma_0(f) = f|_\Gamma$. Fix $\eta > 0$ so that there is a diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$ and $\tilde{c}\eta < 1$, where $\tilde{c}$ is the constant in (5.3.5). By (5.3.22), we see that,

$$\left| \int_{\Omega \setminus \mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon \left| f \right| \, dx \right| \leq \left\| \delta_\varepsilon \right\|_{L^\infty(\Omega \setminus \mathrm{Tub}^\eta(\Gamma))} \left\| f \right\|_{L^1(\Omega)} \to 0 \text{ as } \varepsilon \to 0. \tag{5.3.27}$$

By (5.2.6) with $q_1 = 2$, $q_2 = 1$, we have that,

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon^2} \delta\left(\frac{\eta}{\varepsilon}\right) = 0.$$

Let $C_{\sup,\eta} := \sup_{\varepsilon \in (0,1]} \frac{1}{\varepsilon} \delta_\varepsilon(\eta) < \infty$. Then,

$$\delta\left(\frac{\eta}{\varepsilon}\right) \leq C_{\sup,\eta} \varepsilon^2,$$

and so, we have by (5.2.5),

$$\int_{\frac{\eta}{\varepsilon}}^\infty \delta(s) \, ds \leq \sqrt{\delta\left(\frac{\eta}{\varepsilon}\right)} \left(\int_{\frac{\eta}{\varepsilon}}^\infty \sqrt{\delta(s)} \, ds \right) \leq \sqrt{C_{\sup,\eta}} C_{\delta,\mathrm{int}} \varepsilon \leq C\varepsilon, \tag{5.3.28}$$

for some constant $C > 0$. By (5.3.6) and a change of variable $t = \varepsilon\tilde{t}$,

$$\begin{aligned} &\left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f) \, d\mathcal{H} \right| \qquad (5.3.29) \\ &\leq \int_{\mathbb{R}} \int_\Gamma \delta(\tilde{t}) \left| \chi_{(\frac{-\eta}{\varepsilon}, \frac{\eta}{\varepsilon})}(\tilde{t}) f(p + \varepsilon\tilde{t}\nu(p)) \left| 1 + \varepsilon\tilde{t} C_H(p) + C_R(p, \varepsilon\tilde{t}) \right| - f(p) \right| \, d\mathcal{H} \, d\tilde{t}. \end{aligned}$$

By the fundamental theorem of calculus and Hölder's inequality, for $q < \infty$, we have

$$\begin{aligned} \left| f(p + \varepsilon\tilde{t}\nu(p)) - f(p) \right| &= \left| \int_0^{\tilde{t}} \frac{d}{dt} f(p + \varepsilon\zeta\nu(p)) \, d\zeta \right| = \varepsilon \left| \int_0^{\tilde{t}} \nabla f(p + \varepsilon\zeta\nu(p)) \cdot \nu(p) \, d\zeta \right| \\ &\leq \varepsilon \left| \tilde{t} \right|^{\frac{q-1}{q}} \left(\int_0^{\tilde{t}} \left| \nabla f(p + \varepsilon\zeta\nu(p)) \right|^q \, d\zeta \right)^{\frac{1}{q}}. \end{aligned} \tag{5.3.30}$$

Then, from (5.3.29), we have by Hölder's inequality and (5.3.5),

$$
\begin{aligned}
&\left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f) \, d\mathcal{H} \right| \\
&\leq \int_{\mathbb{R}} \int_\Gamma \left| 1 - \chi_{(\frac{-\eta}{\varepsilon}, \frac{\eta}{\varepsilon})}(\tilde{t}) \left| 1 + \varepsilon \tilde{t} C_H(p) + C_R(p, \varepsilon \tilde{t}) \right| \right| \delta(\tilde{t}) \left| f(p) \right| \, d\mathcal{H} \, d\tilde{t} \\
&+ \varepsilon \int_{\mathbb{R}} \int_\Gamma \chi_{(\frac{-\eta}{\varepsilon}, \frac{\eta}{\varepsilon})}(\tilde{t}) \left| 1 + \varepsilon \tilde{t} C_H(p) + C_R(p, \varepsilon \tilde{t}) \right| \delta(\tilde{t}) \left| \tilde{t} \right|^{\frac{q-1}{q}} \left(\int_0^{\tilde{t}} \left| \nabla f(p + \varepsilon \zeta \nu(p)) \right|^q \, d\zeta \right)^{\frac{1}{q}} \, d\mathcal{H} d\tilde{t} \\
&\leq \left\| \gamma_0(f) \right\|_{L^1(\Gamma)} \int_{\mathbb{R}} \delta(\tilde{t}) \left(\chi_{\mathbb{R} \setminus (\frac{-\eta}{\varepsilon}, \frac{\eta}{\varepsilon})}(\tilde{t}) + \varepsilon \tilde{c} \left| \tilde{t} \right| \right) \, d\tilde{t} \\
&+ \varepsilon (1 + \tilde{c}\eta) \left| \Gamma \right|^{\frac{q-1}{q}} \int_{\mathbb{R}} \delta(\tilde{t}) (1 + \left| \tilde{t} \right|) \left(\int_\Gamma \int_0^{\frac{\eta}{\varepsilon}} \left| \nabla f(p + \varepsilon \zeta \nu(p)) \right|^q \, d\zeta d\mathcal{H} \right)^{\frac{1}{q}} \, d\tilde{t}.
\end{aligned}
$$

By the change of variable $t = \varepsilon\zeta$ and (5.3.7), we observe that,

$$
\left(\int_\Gamma \int_0^{\frac{\eta}{\varepsilon}} \left| \nabla f(p + \varepsilon \zeta \nu(p)) \right|^q \, d\zeta d\mathcal{H} \right)^{\frac{1}{q}} \leq C(\tilde{c}\eta) \varepsilon^{-\frac{1}{q}} \left(\int_{\mathrm{Tub}^\eta(\Gamma)} \left| \nabla f \right|^q \, dx \right)^{\frac{1}{q}},
$$

and so by (5.3.28), and (5.2.5), we have

$$
\begin{aligned}
\left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f) \, d\mathcal{H} \right| &\leq \varepsilon C \left\| \gamma_0(f) \right\|_{L^1(\Gamma)} + \varepsilon^{\frac{q-1}{q}} C \left\| \nabla f \right\|_{L^q(\mathrm{Tub}^\eta(\Gamma))} \\
&\leq C \varepsilon^{\frac{q-1}{q}} \left\| f \right\|_{W^{1,q}(\Omega)}.
\end{aligned}
$$

Similarly, if $q = \infty$, we have

$$
\begin{aligned}
\left| f(p + \varepsilon \tilde{t} \nu(p)) - f(p) \right| &= \varepsilon \left| \int_0^{\tilde{t}} \nabla f(p + \varepsilon \zeta \nu(p)) \cdot \nu(p) \, d\zeta \right| \\
&\leq \varepsilon \left| \tilde{t} \right| \max_{\zeta \in [0, \tilde{t}]} \left| \nabla f(p + \varepsilon \zeta \nu(p)) \right| \leq \varepsilon \left| \tilde{t} \right| \left\| \nabla f \right\|_{C^0(\mathrm{Tub}^\eta(\Gamma))},
\end{aligned}
$$

and hence,

$$
\begin{aligned}
\left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f) \, d\mathcal{H} \right| &\leq \left\| \gamma_0(f) \right\|_{L^1(\Gamma)} \int_{\mathbb{R}} \delta(\tilde{t}) \left(\chi_{\mathbb{R} \setminus (\frac{-\eta}{\varepsilon}, \frac{\eta}{\varepsilon})}(\tilde{t}) + \varepsilon \tilde{c} \left| \tilde{t} \right| \right) \, d\tilde{t} \\
&+ \varepsilon (1 + \tilde{c}\eta) \left| \Gamma \right| \left\| \nabla f \right\|_{C^0(\mathrm{Tub}^\eta(\Gamma)} \int_{\mathbb{R}} \delta(\tilde{t}) \left| \tilde{t} \right| \, d\tilde{t} \\
&\leq C \varepsilon \left\| f \right\|_{C^1(\Omega)}.
\end{aligned}
$$

Together with (5.3.27), (5.3.24) holds true for all $C^1(\Omega)$ functions. Let $\zeta > 0$ be arbitrary, then for any $f \in W^{1,1}(\Omega)$, there exists $g \in C^1(\overline{\Omega})$ such that

$$\|f - g\|_{W^{1,1}(\Omega)} < \zeta, \quad \left| \int_\Omega \delta_\varepsilon g \, dx - \int_\Gamma \gamma_0(g) \, d\mathcal{H} \right| < \zeta.$$

Then, by Lemma 5.21,

$$\begin{aligned}
&\left| \int_\Omega \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f) \, d\mathcal{H} \right| \\
\leq &\left| \int_\Omega \delta_\varepsilon (f-g) \, dx - \int_\Gamma \gamma_0(f-g) \, d\mathcal{H} \right| + \left| \int_\Omega \delta_\varepsilon g \, dx - \int_\Gamma \gamma_0(g) \, d\mathcal{H} \right| \\
\leq &\, C \|f - g\|_{W^{1,1}(\Omega)} + \zeta \leq (C+1)\zeta.
\end{aligned}$$

Since ζ is arbitrary, we see that (5.3.24) holds for any $f \in W^{1,1}(\Omega)$.

We now suppose that $f \in C^1(\overline{\Omega})$ and $f|_\Gamma = 0$. Then, a similar calculation to (5.3.30) yields that

$$\begin{aligned}
\left| f(p + \varepsilon \tilde{t} \nu(p)) \right|^2 &\leq \varepsilon^2 \left| \int_0^{\tilde{t}} |\nabla f(p + \varepsilon \zeta \nu(p))|^2 \, d\zeta \right| \\
&\leq \varepsilon^2 \left| \tilde{t} \right|^{\frac{q-2}{q}} \left(\int_0^{\tilde{t}} |\nabla f(p + \varepsilon \zeta \nu(p))|^q \, d\zeta \right)^{\frac{2}{q}}.
\end{aligned}$$

Hence, by Hölder's inequality and a change of variables $t = \varepsilon\zeta$,

$$\begin{aligned}
&\left| \int_{\mathrm{Tub}^\eta(\Gamma)} \delta_\varepsilon |f|^2 \, dx \right| \\
&\leq \varepsilon^2 \int_{\mathbb{R}} \int_\Gamma \chi_{(\frac{-\eta}{\varepsilon}, \frac{\eta}{\varepsilon})}(\tilde{t}) \left| 1 + \varepsilon \tilde{t} C_H(p) + C_R(p, \varepsilon \tilde{t}) \right| \delta(\tilde{t}) \left| \tilde{t} \right|^{\frac{q-2}{q}} \left(\int_0^{\tilde{t}} |\nabla f(p + \varepsilon \zeta \nu(p))|^q \, d\zeta \right)^{\frac{2}{q}} d\mathcal{H} d\tilde{t} \\
&\leq \varepsilon^2 (1 + \tilde{c}\eta) |\Gamma|^{\frac{q-2}{q}} \left(\int_\Gamma \int_0^{\frac{\eta}{\varepsilon}} |\nabla f(p + \varepsilon \zeta \nu(p))|^q \, d\zeta d\mathcal{H} \right)^{\frac{2}{q}} \left(\int_{\mathbb{R}} \delta(\tilde{t})(1 + |\tilde{t}|) d\tilde{t} \right) \\
&\leq C \varepsilon^{2\frac{q-1}{q}} \|f\|^2_{W^{1,q}(\Omega)}.
\end{aligned}$$

By the density of $C^1(\Omega)$ in $W^{1,q}(\Omega)$, we see that (5.3.26) holds for any $f \in W^{1,q}(\Omega)$ with $\gamma_0(f) = 0$. □

For the double-obstacle regularisation, we note that, by definition

$$\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \delta(\tilde{t})\, d\tilde{t} = 1,$$

and so, by (5.3.30) and (5.3.5), we observe that

$$\begin{aligned}
&\left| \int_{\mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma)} \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f)\, d\mathcal{H} \right| \\
&\leq \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \int_\Gamma \delta(\tilde{t}) \left| f(p+\varepsilon\tilde{t}\nu(p)) \left|1+\varepsilon\tilde{t}C_H(p)+C_R(p,\varepsilon\tilde{t})\right| - f(p) \right| \, d\mathcal{H}d\tilde{t} \\
&\leq \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \int_\Gamma \delta(\tilde{t}) (\left| f(p+\varepsilon\tilde{t}\nu(p)) - f(p) \right| + \left| f(p+\varepsilon\tilde{t}\nu(p) \right| \left| \varepsilon\tilde{t}C_H(p)+C_R(p,\varepsilon\tilde{t}) \right|) \, d\mathcal{H}d\tilde{t} \\
&\leq \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \int_\Gamma \delta(\tilde{t})(1+\varepsilon\tilde{c}\tfrac{\pi}{2})\varepsilon \left|\tilde{t}\right|^{\frac{q-1}{q}} \left(\int_0^{\tilde{t}} |\nabla f(p+\varepsilon\zeta\nu(p))|^q \, d\zeta \right)^{\frac{1}{q}} + \varepsilon\tilde{c}\tfrac{\pi}{2}\delta(\tilde{t}) \left| f(p) \right| \, d\mathcal{H}d\tilde{t} \\
&\leq C\varepsilon \left\| \gamma_0(f) \right\|_{L^1(\Gamma)} + C(1+\tfrac{\pi}{2}\tilde{c}\varepsilon)\varepsilon^{1-\frac{1}{q}} \left\| \nabla f \right\|_{L^q(\Omega)} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \delta(\tilde{t})(1+\left|\tilde{t}\right|) \, d\tilde{t} \\
&\leq C\varepsilon^{1-\frac{1}{q}} \left\| f \right\|_{W^{1,q}(\Omega)},
\end{aligned}$$

for $q < \infty$. Via a similar argument, we also have

$$\left| \int_{\mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma)} \delta_\varepsilon f \, dx - \int_\Gamma \gamma_0(f)\, d\mathcal{H} \right| \leq C\varepsilon \left\| f \right\|_{C^1(\Omega)}.$$

The analogous assertions for the double-obstacle regularisation follow along the same lines as in the proof of Lemma 5.25.

Using (5.2.7), we have

$$\delta_\varepsilon(x) = \frac{1}{\varepsilon}\delta\left(\frac{d(x)}{\varepsilon}\right) \leq \frac{1}{\varepsilon}\frac{1}{C_\xi}\xi\left(\frac{d(x)}{\varepsilon}\right) = \frac{1}{\varepsilon}\frac{1}{C_\xi}\xi_\varepsilon(x). \tag{5.3.31}$$

This implies the following:

Corollary 5.23. *Suppose that ξ_ε and δ_ε satisfy Assumptions 5.6 and 5.7. Then for all $\varepsilon \in (0,1]$ and any $f \in L^2(\Omega, \xi_\varepsilon)$, we have*

$$\int_\Omega \delta_\varepsilon \left| f \right|^2 \, dx \leq \frac{1}{\varepsilon}\frac{1}{C_\xi} \int_\Omega \xi_\varepsilon \left| f \right|^2 \, dx.$$

We introduce the following weighted Sobolev space:

Definition 5.24.

$$L^2(\Gamma\times\mathbb{R},\delta) := \left\{ f:\Gamma\times\mathbb{R}\to\mathbb{R} \text{ measurable s.t } \int_{\mathbb{R}}\int_{\Gamma}\delta(z)\,|f(p,z)|^2\ d\mathcal{H}dz<\infty \right\}.$$

Lemma 5.25. *Suppose Assumptions 5.1, 5.6, and 5.7 are satisfied. Let $\varphi\in H^1(\Omega)$ and $u^\varepsilon\in\mathcal{V}_\varepsilon$. Suppose there exists a constant C, independent of ε, such that, for all $\varepsilon\in(0,1]$,*

$$\|u^\varepsilon\|^2_{1,\xi_\varepsilon}+\|u^\varepsilon\|^2_{0,\delta_\varepsilon}\le C.$$

Then there exists $\tilde{u}\in H^1(\Omega^{(1)})$ such that $u^\varepsilon|_{\Omega^{(1)}}$ converges weakly to $\tilde{u}$ in $H^1(\Omega^{(1)})$ along a subsequence, and for $\varphi\in H^1(\Omega)$,

$$\int_\Omega \delta_\varepsilon u^\varepsilon\varphi\,dx\to\int_\Gamma\gamma_0(\tilde{u})\gamma_0(\varphi)\,d\mathcal{H}\ \text{ as } \varepsilon\to 0. \tag{5.3.32}$$

Proof. The weak convergence of $u^\varepsilon|_{\Omega^{(1)}}$ to $\tilde{u}\in H^1(\Omega^{(1)})$ is proved in Lemma 5.20. Fix $\eta>0$ so that there is a diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma\times(-\eta,\eta)$, and $\tilde{c}\eta<1$, where $\tilde{c}$ is the constant in (5.3.5). We consider the scaled tubular neighbourhood $X^\varepsilon=\mathrm{Tub}^{\varepsilon^k\eta}(\Gamma)$, $0<k<1$, and then by (5.2.6) with $q_1=1, q_2=1-k$, we see that

$$\|\delta_\varepsilon\|_{L^\infty(\Omega\setminus X^\varepsilon)}\to 0 \text{ as } \varepsilon\to 0, \tag{5.3.33}$$

and thus, by Cauchy–Schwarz inequality,

$$\begin{aligned}\left|\int_{\Omega\setminus X^\varepsilon}\delta_\varepsilon u^\varepsilon\varphi\,dx\right| &\le \|u^\varepsilon\|_{L^2(\Omega\setminus X^\varepsilon,\delta_\varepsilon)}\,\|\delta_\varepsilon\|^{\frac12}_{L^\infty(\Omega\setminus X^\varepsilon)}\,\|\varphi\|_{L^2(\Omega\setminus X^\varepsilon)}\\ &\le C\,\|\delta_\varepsilon\|^{\frac12}_{L^\infty(\Omega\setminus X^\varepsilon)}\,\|\varphi\|_{L^2(\Omega)}\to 0 \text{ as } \varepsilon\to 0.\end{aligned} \tag{5.3.34}$$

Hence, it suffices to look at the integral over X^ε. Let $U^\varepsilon(p,z),\Phi_\varepsilon(p,z)$ denote the representations of $u^\varepsilon(x)$ and $\varphi(x)$ in the (p,z) coordinate system, respectively. Then

$$\int_{X^\varepsilon}\delta_\varepsilon u^\varepsilon\varphi\,dx=\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}}\int_\Gamma\delta(z)(U^\varepsilon\Phi_\varepsilon)(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\ d\mathcal{H}dz. \tag{5.3.35}$$

By (5.3.31), (5.3.17) and (5.3.5), $u^\varepsilon \in H^1(\Omega, \xi_\varepsilon)$ implies that

$$\begin{aligned} C &\geq \|u^\varepsilon\|^2_{1,\xi_\varepsilon} \geq \int_{X^\varepsilon} \xi_\varepsilon \left|\nabla u^\varepsilon\right|^2 \, dx \geq \int_{X^\varepsilon} \varepsilon C_\xi \delta_\varepsilon \left|\nabla u^\varepsilon\right|^2 \, dx \\ &\geq \int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_\Gamma \varepsilon C_\xi \delta(z) \frac{1}{\varepsilon^2} \left|\partial_z U^\varepsilon\right|^2 \left|1 + \varepsilon z \mathcal{C}_H(p) + \mathcal{C}_R(p, \varepsilon z)\right| \, d\mathcal{H} dz \\ &\geq C_\xi (1 - \tilde{c}\eta) \int_{\mathbb{R}} \int_\Gamma \chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) \delta(z) \frac{1}{\varepsilon} \left|\partial_z U^\varepsilon\right|^2 (p, z) \, d\mathcal{H} dz. \end{aligned} \tag{5.3.36}$$

From this, we deduce that

$$\chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) \partial_z U^\varepsilon(p, z) \to 0 \text{ in } L^2(\Gamma \times \mathbb{R}, \delta) \text{ as } \varepsilon \to 0. \tag{5.3.37}$$

Similarly, since $\varphi \in H^1(\Omega)$, by (5.3.17),

$$\begin{aligned} \|\varphi\|^2_{H^1(\Omega)} &\geq \int_{X^\varepsilon} |\nabla \varphi|^2 \, dx \geq \frac{1}{\delta(0)} \int_{X^\varepsilon} \varepsilon \delta_\varepsilon \left|\nabla \varphi\right|^2 \, dx \\ &\geq \frac{1 - \tilde{c}\eta}{\delta(0)} \int_{\mathbb{R}} \int_\Gamma \chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) \delta(z) \frac{1}{\varepsilon} \left|\partial_z \Phi_\varepsilon\right|^2 (p, z) \, d\mathcal{H} dz, \end{aligned}$$

and so

$$\chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) \partial_z \Phi_\varepsilon(p, z) \to 0 \text{ in } L^2(\Gamma \times \mathbb{R}, \delta) \text{ as } \varepsilon \to 0. \tag{5.3.38}$$

Since $u^\varepsilon \in L^2(\Omega, \delta_\varepsilon)$, we have

$$\begin{aligned} C &\geq \|u^\varepsilon\|^2_{0,\delta_\varepsilon} \geq \int_{X^\varepsilon} \delta_\varepsilon \left|u^\varepsilon\right|^2 \, dx \\ &\geq (1 - \tilde{c}\eta) \int_{\mathbb{R}} \int_\Gamma \chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) \delta(z) \left|U^\varepsilon\right|^2 (p, z) \, d\mathcal{H} dz. \end{aligned} \tag{5.3.39}$$

Hence, by reflexive weak compactness theorem, there exists $\overline{u} \in L^2(\Gamma \times \mathbb{R}, \delta)$ such that

$$\chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) U^\varepsilon(p, z) \rightharpoonup \overline{u}(p, z) \text{ in } L^2(\Gamma \times \mathbb{R}, \delta) \text{ as } \varepsilon \to 0$$

along a subsequence. By (5.3.37) we can deduce that $\partial_z \overline{u} = 0$ on $J := \{z \in \mathbb{R} : \delta(z) > 0\}$ and hence $\overline{u} = \overline{u}(p)$ in J. Indeed, for any $\Psi = \Psi(p, z)$ that is smooth and compactly supported in J, we have

$$\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_\Gamma \delta(z) (\partial_z U^\varepsilon \Psi)(p, z) \, d\mathcal{H} dz \to 0 \text{ as } \varepsilon \to 0,$$

and

$$\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_\Gamma \delta(z)(\partial_z U^\varepsilon \Psi)(p,z)\, d\mathcal{H}dz = -\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_\Gamma \delta\frac{\delta'}{\delta}(U^\varepsilon\Psi) + \delta(\partial_z\Psi_i U^\varepsilon)\, d\mathcal{H}dz$$
$$\to\ -\int_{\mathbb{R}}\int_\Gamma \delta'\overline{u}\Psi + \delta\overline{u}\partial_z\Psi\, d\mathcal{H}dz = \int_{\mathbb{R}}\int_\Gamma \delta(z)(\partial_z\overline{u}\Psi)(p,z)\, d\mathcal{H}dz \text{ as } \varepsilon\to 0.$$

Hence, for arbitrary Ψ that is smooth and compactly supported in J, we have

$$\int_{\mathbb{R}}\int_\Gamma \delta(z)(\partial_z\overline{u}\Psi)(p,z)\, d\mathcal{H}dz = 0, \tag{5.3.40}$$

which implies that $\partial_z\overline{u} = 0$ in J.

We will show that

$$\int_{X^\varepsilon} \delta_\varepsilon u^\varepsilon\varphi\, dx \to \int_\Gamma \overline{u}\gamma_0(\varphi)\, d\mathcal{H} \text{ as } \varepsilon\to 0, \tag{5.3.41}$$

and then show the identification

$$\overline{u} = \gamma_0(\tilde{u}) \text{ a.e. on } \Gamma. \tag{5.3.42}$$

By (5.3.5) and the definition of Φ_ε, for almost every $(p,z)\in\Gamma\times\mathbb{R}$, as $\varepsilon\to 0$,

$$\chi_{(\frac{-\eta}{\varepsilon^{1-k}},\frac{\eta}{\varepsilon^{1-k}})}(z)\Phi_\varepsilon(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|^{\frac{1}{2}} \to \gamma_0(\varphi)(p). \tag{5.3.43}$$

While, by Lemma 5.21,

$$\begin{aligned}&\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_\Gamma \delta(z)\,|\Phi_\varepsilon|^2\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\ d\mathcal{H}dz\\ &= \int_{X^\varepsilon} \delta_\varepsilon\,|\varphi|^2\ dx \le C\,\|\varphi\|^2_{H^1(\Omega)}\,.\end{aligned} \tag{5.3.44}$$

Moreover, by (5.3.33), we observe that the conclusion of Lemma 5.22 still holds if we use X^ε instead of $\mathrm{Tub}^\eta(\Gamma)$. So, as $\varepsilon\to 0$,

$$\begin{aligned}&\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_\Gamma \delta(z)\,|\Phi_\varepsilon|^2\,(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\ d\mathcal{H}dz\\ &= \int_{X^\varepsilon} \delta_\varepsilon\,|\varphi|^2\ dx \to \int_\Gamma |\gamma_0(\varphi)|^2\ d\mathcal{H} = \int_{\mathbb{R}}\int_\Gamma \delta(z)\,|\gamma_0(\varphi)|^2\,(p)\, d\mathcal{H}dz.\end{aligned} \tag{5.3.45}$$

Almost everywhere convergence (5.3.43) and uniform boundedness of the norm (5.3.44) imply weak convergence in $L^2(\Gamma\times\mathbb{R},\delta)$ (see Theorem C.12). Together with

the norm convergence (5.3.45), this then yields the strong convergence in $L^2(\Gamma\times\mathbb{R},\delta)$ (see Theorem C.13): As $\varepsilon\to 0$,

$$\chi_{(\frac{-\eta}{\varepsilon^{1-k}},\frac{\eta}{\varepsilon^{1-k}})}(z)\Phi_\varepsilon(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|^{\frac{1}{2}}\to\gamma_0(\varphi)(p)\text{ in }L^2(\Gamma\times\mathbb{R},\delta). \tag{5.3.46}$$

By (5.3.5),

$$\sup_{p\in\Gamma,z\in(\frac{-\eta}{\varepsilon^{1-k}},\frac{\eta}{\varepsilon^{1-k}})}|\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\le\tilde{c}\varepsilon^k\eta, \tag{5.3.47}$$

and hence, as $\varepsilon\to 0$,

$$\begin{aligned}\operatorname*{ess\,sup}_{(p,z)}\left||1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|^{\frac{1}{2}}-1\right|&\le\operatorname*{ess\,sup}_{(p,z)}\frac{\tilde{c}\varepsilon^k\eta}{\sqrt{1+\tilde{c}\varepsilon^k\eta}+1}\\&\le C\varepsilon^k\eta\to 0.\end{aligned} \tag{5.3.48}$$

By the product of weak-strong convergence, we see that

$$\begin{aligned}\int_{X^\varepsilon}\delta_\varepsilon u^\varepsilon\varphi\,dx&=\int_{\mathbb{R}}\int_\Gamma\delta(z)\chi_{(\frac{-\eta}{\varepsilon^{1-k}},\frac{\eta}{\varepsilon^{1-k}})}(z)(U^\varepsilon\Phi_\varepsilon)(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\;d\mathcal{H}dz\\&\to\int_{\mathbb{R}}\delta(z)\int_\Gamma\overline{u}(p)\gamma_0(\varphi)(p)\,d\mathcal{H}dz=\int_\Gamma\overline{u}\gamma_0(\varphi)\,d\mathcal{H}\text{ as }\varepsilon\to 0.\end{aligned} \tag{5.3.49}$$

It remains to identify $\overline{u}$ with $\gamma_0(\tilde{u})$. We remark that for $\varepsilon<1$, $\frac{\eta}{\varepsilon^{1-k}}>\eta$ and so the weak convergence of U^ε to $\overline{u}$ also holds in $L^2(\Gamma\times(-\eta,\eta),\delta)$, which is equivalent to restricting to $\mathrm{Tub}^{\varepsilon\eta}(\Gamma)$. Indeed, for any $\Phi\in L^2(\Gamma\times\mathbb{R},\delta)$, we have

$$\left|\int_{-\eta}^{\eta}\int_\Gamma\delta(z)(U^\varepsilon-\overline{u})\Phi\,d\mathcal{H}dz\right|=\left|\int_{\mathbb{R}}\int_\Gamma\delta(z)(U^\varepsilon-\overline{u})\chi_{(-\eta,\eta)}(z)\Phi\,d\mathcal{H}dz\right|\to 0\text{ as }\varepsilon\to 0.$$

Let $C_\eta:=\int_{-\eta}^{\eta}\delta(z)\,dz$ and a similar argument as using (5.3.43), (5.3.44) and (5.3.45) as above shows that, as $\varepsilon\to 0$,

$$\chi_{(-\eta,\eta)}(z)\Phi_\varepsilon(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|^{\frac{1}{2}}\to\gamma_0(\varphi)(p)\chi_{(-\eta,\eta)}(z)\text{ in }L^2(\Gamma\times\mathbb{R},\delta). \tag{5.3.50}$$

By the Cauchy–Schwarz inequality and Lemma 5.21,

$$\begin{aligned}
&\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)\,|\gamma_0(\tilde{u})(p)\Phi_\varepsilon(p,z)|\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_H(p,\varepsilon z)|\;d\mathcal{H}dz\\
&\leq\left(\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)\,|\gamma_0(\tilde{u})|^2\,(p)(1+\tilde{c}\varepsilon\,|z|)\;d\mathcal{H}dz\right)^{\frac{1}{2}}\|\varphi\|_{0,\delta_\varepsilon}\\
&\leq(1+\varepsilon\tilde{c}C_{\delta,\mathrm{int}})^{\frac{1}{2}}\,\|\gamma_0(\tilde{u})\|_{L^2(\Gamma)}\,\|\varphi\|_{0,\delta_\varepsilon}\leq C\,\|\gamma_0(\tilde{u})\|_{L^2(\Gamma)}\,\|\varphi\|_{H^1(\Omega)}\,.
\end{aligned}$$

So, we can compute

$$\begin{aligned}
&\left|\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)(U^\varepsilon(p,z)-\gamma_0(\tilde{u})(p))\Phi_\varepsilon(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\;d\mathcal{H}dz\right|\\
&\leq\left|\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)(U^\varepsilon(p,0)-\gamma_0(\tilde{u})(p))\Phi_\varepsilon(p,0))\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\;d\mathcal{H}dz\right|\\
&+\left|\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)\Big(\int_0^z\partial_\zeta(U^\varepsilon\Phi_\varepsilon(p,\zeta))\;d\zeta\Big)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\;d\mathcal{H}dz\right|\\
&\leq(1+\tilde{c}C_{\delta,\mathrm{int}})\int_{\Gamma}|(\gamma_0(u^\varepsilon)-\gamma_0(\tilde{u}))|\,|\gamma_0(\varphi)|\;d\mathcal{H}\\
&+(1+\tilde{c}\eta)\int_{-\eta}^{\eta}\delta(z)\int_{\Gamma}\int_{-\eta}^{\eta}|\partial_\zeta(U^\varepsilon\Phi_\varepsilon)(p,\zeta)|\;d\zeta\;d\mathcal{H}dz. \qquad (5.3.51)
\end{aligned}$$

The first term on the right hand side converges to zero by the strong convergence of $\gamma_0(u^\varepsilon)$ to $\gamma_0(\tilde{u})$ in $L^2(\Gamma)$ (see Theorem C.5). For the second term, we observe that

$$\begin{aligned}
&\int_{-\eta}^{\eta}\delta(z)\int_{\Gamma}\int_{-\eta}^{\eta}\frac{\delta(\zeta)}{\delta(\zeta)}\,|\partial_\zeta(U^\varepsilon\Phi_\varepsilon)|\,(p,\zeta)\;d\zeta d\mathcal{H}dz\leq\frac{C_\eta}{\delta(\eta)}\int_{\Gamma}\int_{-\eta}^{\eta}\delta(\zeta)\,|\partial_\zeta(U^\varepsilon\Phi_\varepsilon)|\,(p,\zeta)\;d\zeta d\mathcal{H}\\
&\leq\frac{C_\eta}{\delta(\eta)}(\|\partial_zU^\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}\,\|\Phi_\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}+\|U^\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}\,\|\partial_z\Phi_\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}).
\end{aligned}$$

By Lemma 5.21, $\varphi\in L^2(\Omega,\delta_\varepsilon)$ and so by (5.3.39), both $\|U^\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}$ and $\|\Phi^\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}$ are bounded. Hence, by (5.3.37) and (5.3.38), we have

$$\|\partial_zU^\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}\,\|\Phi_\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}+\|U^\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}\,\|\partial_z\Phi_\varepsilon\|_{L^2(\Gamma\times(-\eta,\eta),\delta)}\to0,$$

as $\varepsilon\to0$. As a consequence, from (5.3.51), we have

$$\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)(U^\varepsilon(p,z)-\gamma_0(\tilde{u})(p))\Phi_\varepsilon(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\;d\mathcal{H}dz\to0\text{ as }\varepsilon\to0.$$

But, by (5.3.48) and (5.3.50),

$$\begin{aligned}&\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)\gamma_0(\tilde{u})(p)\Phi_\varepsilon(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\;d\mathcal{H}dz\\ \to&\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)\gamma_0(\tilde{u})(p)\gamma_0(\varphi)(p)\;d\mathcal{H}dz=C_\eta\int_{\Gamma}\gamma_0(\tilde{u})(p)\gamma_0(\varphi)(p)\;d\mathcal{H}\text{ as }\varepsilon\to 0.\end{aligned}$$

Together with the weak convergence of U^ε to $\overline{u}$ in $L^2(\Gamma\times\mathbb{R},\delta)$, we see that

$$\begin{aligned}&\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)(U^\varepsilon(p,z)-\gamma_0(\tilde{u})(p))\Phi_\varepsilon(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\;d\mathcal{H}dz\\ \to&\int_{-\eta}^{\eta}\int_{\Gamma}\delta(z)(\overline{u}(p)-\gamma_0(\tilde{u})(p))\gamma_0(\varphi)(p)\;d\mathcal{H}dz=C_\eta\int_{\Gamma}(\overline{u}-\gamma_0(\tilde{u}))\gamma_0(\varphi)\;d\mathcal{H},\end{aligned}$$

as $\varepsilon\to 0$. Hence, we have

$$0=C_\eta\int_{\Gamma}(\overline{u}-\gamma_0(\tilde{u}))\gamma_0(\varphi)\;d\mathcal{H}. \tag{5.3.52}$$

Since $\varphi\in H^1(\Omega)$ is arbitrary, we deduce that $\overline{u}=\gamma_0(\tilde{u})$ almost everywhere on Γ. □

For the double-obstacle regularisation, we choose $X^\varepsilon=\mathrm{Tub}^{\varepsilon\frac{\pi}{2}}(\Gamma)$ and we will have U^ε converging weakly to $\overline{u}=\overline{u}(p)$ in $L^2(\Gamma\times(-\frac{\pi}{2},\frac{\pi}{2}),\delta)$. The estimate (5.3.47) becomes

$$\sup_{p\in\Gamma,z\in(-\frac{\pi}{2},\frac{\pi}{2})}|\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\le\tilde{c}\varepsilon\frac{\pi}{2}.$$

A similar argument with the above elements will show (5.3.41). Furthermore, we restrict to $\mathrm{Tub}^{\varepsilon\frac{\pi}{4}}(\Gamma)$ to show the identification (5.3.42).

Lemma 5.26. *Assume that δ_ε satisfies Assumption 5.7. For each $\varepsilon\in(0,1]$, let $v^\varepsilon\in H^1(\Omega,\delta_\varepsilon)$. Suppose there exists a constant C, independent of ε, such that*

$$\|v^\varepsilon\|^2_{1,\delta_\varepsilon}\le C\text{ for all }\varepsilon\in(0,1].$$

Then there exists $\overline{v}\in H^1(\Gamma)$ such that, for any $\psi\in H^1(\Gamma)$ with extension $\psi^E\in H^1(\Omega)$ as constructed in the proof of Corollary 5.17,

$$\int_\Omega\delta_\varepsilon v^\varepsilon\psi^E\,dx\to\int_\Gamma\overline{v}\psi\;d\mathcal{H},\quad\int_\Omega\delta_\varepsilon\nabla v^\varepsilon\cdot\nabla\psi^E\,dx\to\int_\Gamma\nabla_\Gamma\overline{v}\cdot\nabla_\Gamma\psi\;d\mathcal{H}\text{ as }\varepsilon\to 0.$$

Proof. Let $\eta>0$ be chosen so that $\tilde{c}\eta<1$ and there is a diffeomorphism between

$\mathrm{Tub}^{\eta}(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. Then, invoking the (p, z) coordinate system, we see that

$$\begin{aligned} C &\geq \|v^{\varepsilon}\|^2_{1,\delta_\varepsilon} \geq \int_{X^{\varepsilon}} \delta_\varepsilon (|v^{\varepsilon}|^2 + |\nabla v^{\varepsilon}|^2)\, dx \\ &\geq (1 - \tilde{c}\eta) \int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_{\Gamma} \delta(z) \left(|V^{\varepsilon}|^2 + \frac{1}{\varepsilon^2} |\partial_z V^{\varepsilon}|^2 + \left| \nabla_{\Gamma} V^{\varepsilon} + \nabla^{\Gamma}_{\varepsilon z} V^{\varepsilon} \right|^2 \right) (p, z)\, d\mathcal{H} dz. \end{aligned}$$

Hence, there exists a function $\overline{v} \in L^2(\Gamma \times \mathbb{R}, \delta)$ and a vector-valued function $\boldsymbol{Q} \in (L^2(\Gamma \times \mathbb{R}, \delta))^n$ such that

$$\begin{aligned} \chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) \partial_z V^{\varepsilon}(p, z) &\to 0 \text{ in } L^2(\Gamma \times \mathbb{R}, \delta) \text{ as } \varepsilon \to 0, \\ \chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) V^{\varepsilon}(p, z) &\rightharpoonup \overline{v}(p, z) \text{ in } L^2(\Gamma \times \mathbb{R}, \delta) \text{ as } \varepsilon \to 0, \\ \chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) (\nabla_{\Gamma} V^{\varepsilon} + \nabla^{\Gamma}_{\varepsilon z} V^{\varepsilon})(p, z) &\rightharpoonup \boldsymbol{Q}(p, z) \text{ in } (L^2(\Gamma \times \mathbb{R}, \delta))^n \text{ as } \varepsilon \to 0. \end{aligned}$$

Moreover, we can deduce, via a similar argument to the derivation of (5.3.40), that $\partial_z \overline{v} = 0$ and $\overline{v} = \overline{v}(p)$ in the set J.

We claim that $\boldsymbol{Q} = \nabla_{\Gamma} \overline{v}(p)$. Let $\{W_i \cap \Gamma\}_{i=1}^N$, $W_i \subset \mathbb{R}^n$, denote a finite open cover of Γ with regular parameterisations $\alpha_i : \mathcal{S}_i \to W_i \cap \Gamma$. Let $\{\mu_i\}_{i=1}^N$ denote a partition of unity subordinate to $\{W_i\}_{i=1}^N$. Take $\Psi \in C_c^{\infty}(\Gamma \times \mathbb{R})$, then for any $1 \leq r \leq n$,

$$\int_{\mathbb{R}} \int_{\Gamma} \delta(z) (Q_r \Psi)(p, z)\, d\mathcal{H} dz = \sum_{i=1}^{N} \int_{\mathbb{R}} \int_{\mathcal{S}_i} \mu_i(\alpha_i(s)) \delta(z) (Q_r \Psi)(s, z) \left| \det J_{i,0}(s) \right|\, ds dz.$$

In the (s, z) coordinate system, by definition (see (5.3.13)), we have that

$$\nabla_{\Gamma} V^{\varepsilon}(s, z) + \nabla^{\Gamma}_{\varepsilon z} V^{\varepsilon}(s, z) = \nabla_{\Gamma^{\varepsilon z}} V^{\varepsilon}(s, z).$$

Moreover, since Γ is C^3, the normal ν belongs to the class C^2. This in turn implies that the components of the metric tensor g^{ij} are C^1 functions. So, for any $1 \leq r \leq n$, we have, as $\varepsilon \to 0$,

$$\begin{aligned} &\int_{\mathcal{S}_i} \mu_i(s) \delta(z) ((\nabla_{\Gamma^{\varepsilon z}} V^{\varepsilon})_r \Psi)(s, z) \left| \det J_{i,0}(s) \right|\, ds \\ = &\int_{\mathcal{S}_i} \mu_i(s) \delta(z) \sum_{j=1}^{n-1} g^{jr}(s, z) \partial_{s_j} V^{\varepsilon}(s, z) \partial_{s_r} G_{\varepsilon}(s, z) \Psi(s, z) \left| \det J_{i,0}(s) \right|\, ds \\ = &-\int_{\mathcal{S}_i} \delta(z) \sum_{j=1}^{n-1} \partial_{s_j} \left(g^{jr}(s, z) \mu_i(s) \Psi(s, z) \left| \det J_{i,0}(s) \right| \partial_{s_r} (\alpha_i + \varepsilon z \nu(\alpha_i)) \right) V^{\varepsilon}(s, z)\, ds. \end{aligned}$$

Integrating with respect to z, summing from $i = 1$ to N and passing to the limit as $\varepsilon \to 0$, we obtain

$$\begin{aligned}
&\sum_{i=1}^{N} \int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_{\mathcal{S}_i} \mu_i(s)\delta(z)((\nabla_{\Gamma^{\varepsilon z}} V^\varepsilon)_r \Psi)(s,z) \left|\det J_{i,0}(s)\right| \, dsdz \\
\to & -\sum_{i=1}^{N} \int_{\mathbb{R}} \int_{\mathcal{S}_i} \delta(z) \sum_{j=1}^{n-1} \partial_{s_j} \left(A^{jr}(s)\mu_i(s)\Psi(s,z) \left|\det J_{i,0}(s)\right| \partial_{s_r}\alpha_i \right) \overline{v}(s) \, dsdz \\
= & \sum_{i=1}^{N} \int_{\mathbb{R}} \int_{\mathcal{S}_i} \mu_i(s)\delta(z) \sum_{j=1}^{n-1} A^{jr}(s)\partial_{s_j}\overline{v}(s)\partial_{s_r}\alpha_i(s)\Psi(s,z) \left|\det J_{i,0}(s)\right| \, dsdz \\
= & \int_{\mathbb{R}} \int_{\Gamma} \delta(z)(\nabla_\Gamma \overline{v})_r(p)\Psi(p,z) \, d\mathcal{H}dz.
\end{aligned}$$

Meanwhile, by the weak convergence of $\chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z)(\nabla_{\Gamma^{\varepsilon z}} V^\varepsilon)_r(s,z)$ to $Q_r(s,z)$, we have

$$\begin{aligned}
&\sum_{i=1}^{N} \int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}} \int_{\mathcal{S}_i} \mu_i(s)\delta(z)((\nabla_{\Gamma^{\varepsilon z}} V^\varepsilon)_r \Psi)(s,z) \left|\det J_{i,0}(s)\right| \, dsdz \\
\to & \sum_{i=1}^{N} \int_{\mathbb{R}} \int_{\mathcal{S}_i} \mu_i(s)\delta(z)(Q_r\Psi)(s,z) \left|\det J_{i,0}(s)\right| \, dsdz \text{ as } \varepsilon \to 0.
\end{aligned}$$

Equating the limits leads to

$$\int_{\mathbb{R}} \int_{\Gamma} \delta(z)(Q_r\Psi)(p,z) \, d\mathcal{H}dz = \int_{\mathbb{R}} \int_{\Gamma} \delta(z)(\nabla_\Gamma \overline{v})_r(p)\Psi(p,z) \, d\mathcal{H}dz,$$

and thus $Q_r = (\nabla_\Gamma \overline{v})_r$.

Given $\psi \in H^1(\Gamma)$ and its extension $\psi^E \in H^1(\Omega)$, we observe that the corresponding statements to (5.3.43), (5.3.44), and (5.3.45) with φ replaced by ψ^E are valid. So, (5.3.49) also applies when we replace $u^\varepsilon\varphi$ by $v^\varepsilon\psi^E$. Together with (5.3.34), we have

$$\int_\Omega \delta_\varepsilon v^\varepsilon \psi^E \, dx \to \int_\Gamma \overline{v}\psi \, d\mathcal{H}, \text{ as } \varepsilon \to 0.$$

As ψ^e is constructed by extending ψ constantly in the normal direction, we see that by (5.3.18),

$$0 = \nabla\psi^e(x) \cdot \nu(p(x)) = \frac{1}{\varepsilon^2}\partial_z\Psi_\varepsilon(p,z) + (\nabla_\Gamma\Psi_\varepsilon + \nabla^\Gamma_{\varepsilon z}\Psi_\varepsilon)(p,z) \cdot \nu(p) = \frac{1}{\varepsilon^2}\partial_z\Psi_\varepsilon(p,z),$$

i.e., $\partial_z\Psi_\varepsilon = 0$.

By (5.3.12) we have the almost everywhere convergence: As $\varepsilon \to 0$,

$$\chi_{(\frac{-\eta}{\varepsilon^{1-k}},\frac{\eta}{\varepsilon^{1-k}})}(z)(\nabla_\Gamma \Psi_\varepsilon + \nabla^\Gamma_{\varepsilon z}\Psi_\varepsilon)(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|^{\frac{1}{2}} \to \nabla_\Gamma \psi(p).$$

By Corollary 5.17, we have uniform boundedness of the norm:

$$\begin{aligned}&\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}}\int_\Gamma \delta(z)\left|\nabla_\Gamma \Psi_\varepsilon + \nabla^\Gamma_{\varepsilon z}\Psi_\varepsilon\right|^2 |1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\ d\mathcal{H}dz\\ =&\int_{X^\varepsilon}\delta_\varepsilon\left|\nabla\psi^E\right|^2\ dx \le C\left\|\nabla_\Gamma\psi\right\|^2_{L^2(\Gamma)},\end{aligned}$$

and by (5.3.21), we have the convergence of the norm: As $\varepsilon \to 0$,

$$\begin{aligned}&\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}}\int_\Gamma \delta(z)\left|\nabla_\Gamma \Psi_\varepsilon + \nabla^\Gamma_{\varepsilon z}\Psi_\varepsilon\right|^2 (p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\ d\mathcal{H}dz\\ =&\int_{X^\varepsilon}\delta_\varepsilon\left|\nabla\psi^E\right|^2\ dx \to \int_\Gamma |\nabla_\Gamma\psi|^2\ d\mathcal{H} = \int_{\mathbb{R}}\int_\Gamma \delta(z)\,|\nabla_\Gamma\psi|^2(p)\ d\mathcal{H}dz.\end{aligned}$$

Hence, we have the following strong convergence:

$$\chi_{(\frac{-\eta}{\varepsilon^{1-k}},\frac{\eta}{\varepsilon^{1-k}})}(z)(\nabla_\Gamma \Psi_\varepsilon + \nabla^\Gamma_{\varepsilon z}\Psi_\varepsilon)(p,z)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|^{\frac{1}{2}} \to \nabla_\Gamma \psi(p) \text{ in } L^2(\Gamma\times\mathbb{R},\delta).$$

Then, by the product of weak-strong convergence, we see that

$$\begin{aligned}&\int_{\frac{-\eta}{\varepsilon^{1-k}}}^{\frac{\eta}{\varepsilon^{1-k}}}\int_\Gamma \delta(z)(\nabla_\Gamma V^\varepsilon + \nabla^\Gamma_{\varepsilon z}V^\varepsilon)\cdot(\nabla_\Gamma \Psi_\varepsilon + \nabla^\Gamma_{\varepsilon z}\Psi_\varepsilon)\,|1+\varepsilon z\mathcal{C}_H(p)+\mathcal{C}_R(p,\varepsilon z)|\ d\mathcal{H}dz\\ =&\int_{X^\varepsilon}\delta_\varepsilon\nabla v^\varepsilon\cdot\nabla\psi^e\ dx \to \int_\Gamma \nabla_\Gamma\overline{v}\cdot\nabla_\Gamma\psi\ d\mathcal{H} \text{ as } \varepsilon\to 0.\end{aligned}$$

□

We define

$$H^1_{\Gamma,0}(\Omega) := \{f\in H^1(\Omega) : f|_\Gamma = 0\}.$$

This is a closed subspace of $H^1(\Omega)$ under $\|\cdot\|_{H^1(\Omega)}$ and hence is a Hilbert space itself.

Lemma 5.27. *Suppose δ_ε satisfies Assumption 5.7. Then any for $f \in H^1_{\Gamma,0}(\Omega)$, there exists a constant $C>0$, independent of f and ε, such that*

$$\|f\|_{0,\frac{1}{\varepsilon}\delta_\varepsilon} \le C\|f\|_{H^1(\Omega)}. \tag{5.3.53}$$

Moreover,

$$\int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon \left|f\right|^2 \, dx \to 0 \ \textit{as} \ \varepsilon \to 0. \tag{5.3.54}$$

Proof. Let $\eta > 0$ so that $\tilde{c}\eta < 1$ and there is a diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. By (5.2.6) with $q_1 = 2, q_2 = 1$, we see that

$$\left\|\tfrac{1}{\varepsilon}\delta_\varepsilon\right\|_{L^\infty(\Omega\setminus \mathrm{Tub}^\eta(\Gamma))} \to 0 \text{ as } \varepsilon \to 0.$$

Hence, there exists $C > 0$, independent of $\varepsilon \in (0, 1]$, such that

$$\left\|\tfrac{1}{\varepsilon}\delta_\varepsilon\right\|_{L^\infty(\Omega\setminus \mathrm{Tub}^\eta(\Gamma))} \le C.$$

By (5.3.26) with $q = 2$, we have that

$$\begin{aligned}\int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon \left|f\right|^2 \, dx &\le \int_{\mathrm{Tub}^\eta(\Gamma)} \frac{1}{\varepsilon}\delta_\varepsilon \left|f\right|^2 \, dx + \left\|\tfrac{1}{\varepsilon}\delta_\varepsilon\right\|_{L^\infty(\Omega\setminus \mathrm{Tub}^\eta(\Gamma))} \left\|f\right\|^2_{L^2(\Omega\setminus \mathrm{Tub}^\eta(\Gamma))} \\ &\le C\left\|f\right\|^2_{H^1(\Omega)} + C\left\|f\right\|^2_{L^2(\Omega)} \le C\left\|f\right\|^2_{H^1(\Omega)},\end{aligned}$$

where C is independent of f and ε.

For $g \in C^1(\overline{\Omega})$ with $g|_\Gamma = 0$, we have from (5.3.26) with $q = \infty$,

$$\int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon \left|g\right|^2 \, dx \le C\varepsilon \left\|g\right\|^2_{C^1(\Omega)} + \left\|\tfrac{1}{\varepsilon}\delta_\varepsilon\right\|_{L^\infty(\Omega\setminus \mathrm{Tub}^\eta(\Gamma))} \left\|g\right\|^2_{L^2(\Omega)} \to 0 \text{ as } \varepsilon \to 0.$$

Let $\zeta > 0$ be arbitrary. Then, for any $f \in H^1_{\Gamma,0}(\Omega)$, there exists $g \in C^1(\overline{\Omega})$ with $g|_\Gamma = 0$ such that

$$\left\|f - g\right\|^2_{H^1(\Omega)} < \zeta, \quad \int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon \left|g\right|^2 \, dx \le \zeta.$$

Then, by (5.3.53),

$$\begin{aligned}\int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon \left|f\right|^2 \, dx &\le \int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon \left|f - g\right|^2 \, dx + \int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon \left|g\right|^2 \, dx \\ &\le C\left\|f - g\right\|^2_{H^1(\Omega)} + \zeta \le (C+1)\zeta.\end{aligned}$$

As ζ is arbitrary, we see that (5.3.54) holds for any $f \in H^1_{\Gamma,0}(\Omega)$. □

5.4 Proof of the main results

5.4.1 Well-posedness of (CSI)

We consider the product Hilbert space and associated inner product

$$\mathcal{X} := H^1(\Omega^{(1)}) \times H^1(\Gamma),$$
$$\langle (u_1, v_1), (u_2, v_2) \rangle_{\mathcal{X}} := \int_{\Omega^{(1)}} u_1 u_2 + \nabla u_1 \cdot \nabla u_2 \, dx + \int_\Gamma v_1 v_2 + \nabla_\Gamma v_1 \cdot \nabla_\Gamma v_2 \, d\mathcal{H}.$$

The weak formulation for (CSI) is: Find $(u, v) \in \mathcal{X}$ such that for all $(\varphi, \psi) \in \mathcal{X}$,

$$\begin{aligned} a_{CSI}((u, v), (\varphi, \psi)) &:= a_B(u, \varphi) + a_S(v, \psi) + K l_S(v - \gamma_0(u), \psi - \gamma_0(\varphi)) \\ &= l_B(f, \varphi) + \beta l_S(g, \psi) =: l_{CSI}((f, g), (\varphi, \psi)), \end{aligned}$$

where $a_B(\cdot, \cdot)$, $a_S(\cdot, \cdot)$, $l_B(\cdot, \cdot)$ and $l_S(\cdot, \cdot)$ are as defined in Section 5.2.5.

By the root mean square inequality, i.e.,

$$a + b \leq \sqrt{2}\sqrt{a^2 + b^2},$$

one can show that

$$\begin{aligned} |l_{CSI}((\varphi, \psi))| &\leq \|f\|_{L^2(\Omega^{(1)})} \|\varphi\|_{L^2(\Omega^{(1)})} + \|g\|_{L^2(\Gamma)} \|\psi\|_{L^2(\Gamma)} \\ &\leq (\|f\|_{L^2(\Omega^{(1)})} + \|g\|_{L^2(\Gamma)})(\|\varphi\|_{H^1(\Omega^{(1)})} + \|\psi\|_{L^2(\Gamma)}) \\ &\leq \sqrt{2}(\|f\|_{L^2(\Omega^{(1)})} + \|g\|_{L^2(\Gamma)}) \sqrt{\|\varphi\|^2_{H^1(\Omega^{(1)})} + \|\psi\|^2_{L^2(\Gamma)}} \\ &= \sqrt{2}(\|f\|_{L^2(\Omega^{(1)})} + \|g\|_{L^2(\Gamma)}) \, \|(\varphi, \psi)\|_{\mathcal{X}}, \\ \int_\Gamma |(v - \gamma_0(u))(\psi - \gamma_0(\varphi))| \, d\mathcal{H} &\leq \|v - \gamma_0(u)\|_{L^2(\Gamma)} \|\psi - \gamma_0(\varphi)\|_{L^2(\Gamma)} \\ &\leq (\|v\|_{L^2(\Gamma)} + C_{\mathrm{tr}} \|u\|_{H^1(\Omega^{(1)})})(\|\psi\|_{L^2(\Gamma)} + C_{\mathrm{tr}} \|\varphi\|_{H^1(\Omega^{(1)})}) \\ &\leq 2(1 + C^2_{\mathrm{tr}}) \, \|(u, v)\|_{\mathcal{X}} \, \|(\varphi, \psi)\|_{\mathcal{X}}, \end{aligned}$$

and so

$$|a_{CSI}((u, v), (\varphi, \psi))| \leq (C_{\mathcal{A},\mathcal{B},a,b} + 2K(1 + C^2_{\mathrm{tr}})) \, \|(u, v)\|_{\mathcal{X}} \, \|(\varphi, \psi)\|_{\mathcal{X}}.$$

Moreover,

$$\begin{aligned} a_{CSI}((u, v), (u, v)) &\geq \min(\theta_0, \theta_2) \, \|u\|^2_{H^1(\Omega^{(1)})} + \min(\theta_1, \theta_3) \, \|v\|^2_{H^1(\Gamma)} + K \, \|v - \gamma_0(u)\|^2_{L^2(\Gamma)} \\ &\geq (\min_i \theta_i) \, \|(u, v)\|^2_{\mathcal{X}}. \end{aligned}$$

By Lax–Milgram theorem, there exists a unique weak solution $(u, v) \in \mathcal{X}$ to (CSI) such that

$$\|(u,v)\|_{\mathcal{X}} \leq C(\theta_i)(\|f\|_{L^2(\Omega^{(1)})} + \|g\|_{L^2(\Gamma)}).$$

We remark that the well-posedness of (SSI), (RSI), (DSIH), and (NSIH) are shown similarly via the Lax–Milgram theorem, and hence the details are omitted.

5.4.2 Well-posedness of (CDD)

We consider the product Hilbert space and associated inner product

$$\begin{aligned}\mathcal{X}_\varepsilon &:= \mathcal{V}_\varepsilon \times H^1(\Omega, \delta_\varepsilon),\\ \langle (u_1,v_1),(u_2,v_2)\rangle_{\mathcal{X}_\varepsilon} &:= \int_\Omega (\xi_\varepsilon + \delta_\varepsilon) u_1 u_2 + \xi_\varepsilon \nabla u_1 \cdot \nabla u_2 + \delta_\varepsilon v_1 v_2 + \delta_\varepsilon \nabla v_1 \cdot \nabla v_2 \, dx.\end{aligned}$$

The weak formulation for (CDD) is: Find $(u^\varepsilon, v^\varepsilon) \in \mathcal{X}_\varepsilon$ such that for all $(\varphi, \psi) \in \mathcal{X}_\varepsilon$,

$$\begin{aligned}a_{CDD}((u^\varepsilon, v^\varepsilon),(\varphi,\psi)) &:= \int_\Omega \xi_\varepsilon \mathcal{A}^E \nabla u^\varepsilon \cdot \nabla \varphi + \xi_\varepsilon a^E u^\varepsilon \varphi + \delta_\varepsilon \mathcal{B}^E \nabla v^\varepsilon \cdot \nabla \psi + \delta_\varepsilon b^E v^\varepsilon \psi \, dx \\ &\quad + \int_\Omega \delta_\varepsilon K (v^\varepsilon - u^\varepsilon)(\psi - \varphi) \, dx = \int_\Omega \xi_\varepsilon f^E \varphi + \beta \delta_\varepsilon g^E \psi =: l_{CDD}((\varphi,\psi)).\end{aligned}$$

A similar calculation involving the root mean square inequality will show that

$$\begin{aligned}|l_{CDD}((\varphi,\psi))| &\leq \left\|f^E\right\|_{0,\xi_\varepsilon} \|\varphi\|_{1,\xi_\varepsilon} + \left\|g^E\right\|_{0,\delta_\varepsilon} \|\psi\|_{1,\delta_\varepsilon} \\ &\leq \sqrt{2}\Big(\left\|f^E\right\|_{0,\xi_\varepsilon} + \left\|g^E\right\|_{0,\delta_\varepsilon} \Big) \sqrt{\|\varphi\|^2_{1,\xi_\varepsilon} + \|\psi\|^2_{1,\delta_\varepsilon}} \\ &\leq \sqrt{2}\Big(\left\|f^E\right\|_{0,\xi_\varepsilon} + \left\|g^E\right\|_{0,\delta_\varepsilon} \Big) \|(\varphi,\psi)\|_{\mathcal{X}_\varepsilon},\end{aligned}$$

and

$$\begin{aligned}&|a_{CDD}((u,v),(\varphi,\psi))| \\ &\leq C_{\mathcal{A}^E,\mathcal{B}^E,a^E,b^E} \|(u^\varepsilon,v^\varepsilon)\|_{\mathcal{X}_\varepsilon} \|(\varphi,\psi)\|_{\mathcal{X}_\varepsilon} + K(\|v^\varepsilon\|_{0,\delta_\varepsilon} + \|u^\varepsilon\|_{0,\delta_\varepsilon})(\|\psi\|_{0,\delta_\varepsilon} + \|\varphi\|_{0,\delta_\varepsilon}) \\ &\leq (C_{\mathcal{A}^E,\mathcal{B}^E,a^E,b^E} + K) \|(u^\varepsilon,v^\varepsilon)\|_{\mathcal{X}_\varepsilon} \|(\varphi,\psi)\|_{\mathcal{X}_\varepsilon}.\end{aligned}$$

By Young's inequality with constant $\mu \in (1,2)$, we have

$$\begin{aligned}\int_\Omega \delta_\varepsilon |v^\varepsilon - u^\varepsilon|^2 \, dx &\geq \int_\Omega \delta_\varepsilon (|v^\varepsilon|^2 - 2|v^\varepsilon||u^\varepsilon| + |u^\varepsilon|^2) \, dx \\ &\geq (1-\mu)\|v^\varepsilon\|^2_{0,\delta_\varepsilon} + (1-\mu^{-1})\|u^\varepsilon\|^2_{0,\delta_\varepsilon}.\end{aligned}$$

Then, by Assumption 5.2, we have $\theta_3 \geq K$, and so

$$\begin{aligned}
&a_{CDD}((u^\varepsilon, v^\varepsilon), (u^\varepsilon, v^\varepsilon)) \\
&\geq C(\theta_0, \theta_2) \|u^\varepsilon\|^2_{1,\xi_\varepsilon} + \theta_1 \|\nabla v^\varepsilon\|^2_{0,\delta_\varepsilon} + \theta_3 \|v^\varepsilon\|^2_{0,\delta_\varepsilon} + K \|v^\varepsilon - u^\varepsilon\|^2_{0,\delta_\varepsilon} \\
&\geq C \|u^\varepsilon\|^2_{1,\xi_\varepsilon} + \theta_1 \|\nabla v^\varepsilon\|^2_{0,\delta_\varepsilon} + K(2-\mu) \|v^\varepsilon\|^2_{0,\delta_\varepsilon} + K(1-\mu^{-1}) \|u^\varepsilon\|^2_{0,\delta_\varepsilon} \\
&\geq C(\theta_i, K, \mu) \|(u^\varepsilon, v^\varepsilon)\|^2_{\mathcal{X}_\varepsilon}.
\end{aligned}$$

Hence, by the Lax–Milgram theorem, for every $\varepsilon > 0$ there exists a pair of functions $(u^\varepsilon, v^\varepsilon) \in \mathcal{X}_\varepsilon$ that is a weak solution to (CDD) and satisfies

$$\|(u^\varepsilon, v^\varepsilon)\|_{\mathcal{X}_\varepsilon} \leq C\Big(\big\|f^E\big\|_{0,\xi_\varepsilon} + \big\|g^E\big\|_{0,\delta_\varepsilon} \Big).$$

By $\xi_\varepsilon \leq 1$ and Lemma 5.18, there exists a constant C, independent of ε, such that

$$\big\|f^E\big\|^2_{0,\xi_\varepsilon} + \big\|g^E\big\|^2_{0,\delta_\varepsilon} \leq C\Big(\big\|f^E\big\|^2_{L^2(\Omega)} + \big\|g^E\big\|^2_{L^2(\Omega)} \Big).$$

Hence,

$$\|u^\varepsilon\|^2_{1,\xi_\varepsilon} + \|u^\varepsilon\|^2_{0,\delta_\varepsilon} + \|v^\varepsilon\|^2_{1,\delta_\varepsilon} \leq C\Big(\big\|f^E\big\|^2_{L^2(\Omega)} + \big\|g^E\big\|^2_{L^2(\Omega)} \Big),$$

which is (5.2.17).

By a similar argument involving the Lax–Milgram theorem, one can show the well-posedness of (SDD) in $H^1(\Omega, \delta_\varepsilon)$, (RDD) in $\mathcal{V}_\varepsilon$, (DDDH) in $\mathcal{W}_\varepsilon$ and (NDDH) in $H^1(\Omega, \xi_\varepsilon)$. The uniform boundedness in ε of the estimates (5.2.18), (5.2.19), (5.2.20) and (5.2.21) follow from Lemma 5.18 and the property that $\xi_\varepsilon \leq 1$.

5.4.3 Issue of uniform estimates for (NDD)

We define

$$\begin{aligned}
a_{NDD}(u, \phi) &:= \int_\Omega \xi_\varepsilon \mathcal{A}^E \nabla u \cdot \nabla \phi + \xi_\varepsilon a^E u \phi \, dx, \\
l_{NDD}(\phi) &:= \int_\Omega \xi_\varepsilon f^E \phi + \delta_\varepsilon g^E \phi \, dx.
\end{aligned}$$

Suppose we seek weak solutions in the space $H^1(\Omega, \xi_\varepsilon)$, then $a_{NDD}(\cdot, \cdot)$ is bounded and coercive. But, by Corollary 5.23, the boundedness of l_{NDD} over $H^1(\Omega, \xi_\varepsilon)$ scales with $\frac{1}{\varepsilon}$. Thus, we cannot obtain a uniform estimate similar to (5.2.21). If we seek weak solutions in the space $\mathcal{V}_\varepsilon$, then l_{NDD} is bounded uniformly in ε. But a_{NDD} is not coercive. Hence, to obtain uniform estimates in ε, we have to remove the

term involving δ_ε and this amounts to transforming (NSI) into its homogeneous version (NSIH) through Theorem C.7. This then motivates Assumption 5.3 and the corresponding diffuse domain approximation (NDDH) now has a weak solution in $H^1(\Omega, \xi_\varepsilon)$ with uniform estimates in ε.

5.4.4 Convergence of (CDD) to (CSI)

Let $\varphi \in H^1(\Omega^{(1)})$ and $\psi \in H^1(\Gamma)$ be arbitrary. Then by the Extension theorem we can extend φ to a function $\varphi^E \in H^1(\Omega)$. Similarly, we denote by $\psi^E \in H^1(\Omega)$ the extension of ψ to Ω constructed as in the proof of Corollary 5.17.

By $\xi_\varepsilon \leq 1$, Lemma 5.21, and Lemma 5.18, we see that $\varphi^E \in \mathcal{V}_\varepsilon$ and $\psi^E \in H^1(\Omega, \delta_\varepsilon)$ for all $\varepsilon \in (0, 1]$. Moreover,

$$\left\|\varphi^E\right\|_{\mathcal{V}_\varepsilon} \leq C \left\|\varphi\right\|_{H^1(\Omega^{(1)})}, \quad \left\|\psi^E\right\|_{1,\delta_\varepsilon} \leq C \left\|\psi\right\|_{H^1(\Gamma)},$$

where the constant C is independent of ε. Thus, we may test with φ^E and ψ^E in the weak formulation for (CDD).

For $\varepsilon \in (0, 1]$, let $(u^\varepsilon, v^\varepsilon) \in \mathcal{X}_\varepsilon$ denote the unique weak solution to (CDD), which satisfies

$$\begin{aligned}&\int_\Omega \xi_\varepsilon \mathcal{A}^E \nabla u^\varepsilon \cdot \nabla \varphi^E + \xi_\varepsilon a^E u^\varepsilon \varphi^E + \delta_\varepsilon \mathcal{B}^E \nabla v^\varepsilon \cdot \nabla \psi^E + \delta_\varepsilon b^E v^\varepsilon \psi^E \, dx \\ &+ \int_\Omega K \delta_\varepsilon (v^\varepsilon - u^\varepsilon)(\psi^E - \varphi^E) \, dx - \int_\Omega \xi_\varepsilon f^E \varphi^E + \beta \delta_\varepsilon g^E \psi^E \, dx = 0.\end{aligned}$$

We analyse the bulk quantity and the surface quantity separately. From (5.2.17), we have that

$$\|u^\varepsilon\|^2_{1,\xi_\varepsilon} + \|u^\varepsilon\|^2_{0,\delta_\varepsilon} \leq \|(u^\varepsilon, v^\varepsilon)\|^2_{\mathcal{X}_\varepsilon} \leq C\Big(\left\|f^E\right\|^2_{L^2(\Omega)} + \left\|g^E\right\|^2_{L^2(\Omega)} \Big).$$

Hence, by Lemma 5.25, Lemma 5.20, and Rellich–Kondrachov compactness theorem (Theorem C.8), there exists a function $\tilde{u} \in H^1(\Omega^{(1)})$ such that, along a subsequence,

$$\begin{aligned} u^\varepsilon|_{\Omega^{(1)}} &\rightharpoonup \tilde{u} \text{ in } H^1(\Omega^{(1)}) \text{ as } \varepsilon \to 0, \\ u^\varepsilon|_{\Omega^{(1)}} &\to \tilde{u} \text{ in } L^2(\Omega^{(1)}) \text{ as } \varepsilon \to 0, \\ \int_\Omega \delta_\varepsilon u^\varepsilon (\psi^E - \varphi^E) \, dx &\to \int_\Gamma \gamma_0(\tilde{u})(\psi - \gamma_0(\varphi)) \, d\mathcal{H} \text{ as } \varepsilon \to 0. \end{aligned}$$

By Lemma 5.19, we see that

$$\int_\Omega \xi_\varepsilon f^E \varphi^E \, dx = \int_{\Omega^{(1)}} \xi_\varepsilon f\varphi \, dx + \int_{\Omega\setminus\Omega^{(1)}} \xi_\varepsilon f^E \varphi^E \, dx \to \int_{\Omega^{(1)}} f\varphi \, dx \text{ as } \varepsilon \to 0. \tag{5.4.1}$$

Furthermore, by Cauchy–Schwarz inequality, Lemma 5.19, (5.2.17), the strong convergence of $u^\varepsilon|_{\Omega^{(1)}}$ to $\tilde{u}$ in $L^2(\Omega^{(1)})$ and the fact that $\xi_\varepsilon \le 1$ in Ω,

$$\begin{aligned}
&\left| \int_\Omega \xi_\varepsilon a^E u^\varepsilon \varphi^E \, dx - \int_{\Omega^{(1)}} a\tilde{u}\varphi \, dx \right| \le \left| \int_{\Omega^{(1)}} a(\xi_\varepsilon u^\varepsilon - \tilde{u})\varphi \, dx \right| + \left| \int_{\Omega\setminus\Omega^{(1)}} a^E \xi_\varepsilon u^\varepsilon \varphi^E \, dx \right| \\
&\le C_a \left(\int_{\Omega^{(1)}} |\xi_\varepsilon u^\varepsilon - \tilde{u}| \, |\varphi| \, dx + \|u^\varepsilon\|_{L^2(\Omega\setminus\Omega^{(1)},\xi_\varepsilon)} \left\|\varphi^E\right\|_{L^2(\Omega\setminus\Omega^{(1)},\xi_\varepsilon)} \right) \\
&\le C_a \left(\int_{\Omega^{(1)}} |u^\varepsilon - \tilde{u}| \, |\varphi| \, dx + \int_{\Omega^{(1)}} (1-\xi_\varepsilon) \, |\varphi\tilde{u}| \, dx + C_{f,g} \left\|\varphi^E\right\|_{L^2(\Omega\setminus\Omega^{(1)},\xi_\varepsilon)} \right) \to 0,
\end{aligned}$$

as $\varepsilon \to 0$. Thus,

$$\int_\Omega \xi_\varepsilon a^E u^\varepsilon \varphi^E \, dx \to \int_{\Omega^{(1)}} a\tilde{u}\varphi \, dx \text{ as } \varepsilon \to 0. \tag{5.4.2}$$

We note that, by the Cauchy–Schwarz inequality, (5.2.17), Lemma 5.19 and the fact that $\xi_\varepsilon \ge \frac{1}{2}$ in $\Omega^{(1)}$,

$$\begin{aligned}
\int_{\Omega^{(1)}} (1-\xi_\varepsilon) \, |\nabla u^\varepsilon| \, |\nabla\varphi| \, dx &\le \left(\int_{\Omega^{(1)}} \frac{1}{2} \, |\nabla u^\varepsilon|^2 \, dx \right)^{\frac{1}{2}} \left(\int_{\Omega^{(1)}} (1-\xi_\varepsilon) \, |\nabla\varphi|^2 \, dx \right)^{\frac{1}{2}} \\
&\le \|\nabla u^\varepsilon\|_{L^2(\Omega,\xi_\varepsilon)} \left(\int_{\Omega^{(1)}} (1-\xi_\varepsilon) \, |\nabla\varphi|^2 \, dx \right)^{\frac{1}{2}} \\
&\le C_{f,g} \left(\int_{\Omega^{(1)}} (1-\xi_\varepsilon) \, |\nabla\varphi|^2 \, dx \right)^{\frac{1}{2}} \to 0 \text{ as } \varepsilon \to 0.
\end{aligned}$$

Together with the weak convergence of $\nabla u^\varepsilon|_{\Omega^{(1)}}$ to $\nabla\tilde{u}$ in $\Omega^{(1)}$, we obtain

$$\begin{aligned}
&\left| \int_\Omega \xi_\varepsilon \mathcal{A}^E \nabla u^\varepsilon \cdot \nabla\varphi^E \, dx - \int_{\Omega^{(1)}} \mathcal{A}\nabla\tilde{u} \cdot \nabla\varphi \, dx \right| \\
&\le \left| \int_{\Omega^{(1)}} \nabla(u^\varepsilon - \tilde{u}) \cdot \mathcal{A}^T \nabla\varphi \, dx \right| + \|\mathcal{A}\|_{L^\infty(\Omega^{(1)})} \int_{\Omega^{(1)}} (1-\xi_\varepsilon) \, |\nabla u^\varepsilon| \, |\nabla\varphi| \, dx \\
&+ \left| \int_{\Omega\setminus\Omega^{(1)}} \xi_\varepsilon \nabla u^\varepsilon \cdot (\mathcal{A}^E)^T \nabla\varphi^E \, dx \right| \to 0 \text{ as } \varepsilon \to 0,
\end{aligned} \tag{5.4.3}$$

where $\mathcal{A}^T$ denotes the transpose of $\mathcal{A}$.

Hence, as $\varepsilon \to 0$,

$$\begin{aligned}&\int_\Omega \xi_\varepsilon \mathcal{A}^E \nabla u^\varepsilon \cdot \nabla \varphi^E + \xi_\varepsilon a^E u^\varepsilon \varphi^E - \xi_\varepsilon f^E \varphi^E - K\delta_\varepsilon u^\varepsilon(\psi^E - \varphi^E)\, dx \\ \to &\int_{\Omega^{(1)}} \mathcal{A}\nabla \tilde{u} \cdot \nabla \varphi + a\tilde{u}\varphi - f\varphi\, dx - \int_\Gamma K\gamma_0(\tilde{u})(\psi - \gamma_0(\varphi))\, d\mathcal{H}. \end{aligned} \tag{5.4.4}$$

For the surface quantity, we choose the scaled tubular neighbourhood $X^\varepsilon := \mathrm{Tub}^{\varepsilon^k \eta}(\Gamma)$, $0 < k < 1$, where $\eta > 0$ is a constant such that $\tilde{c}\eta < 1$ and there is a diffeomorphism between $\mathrm{Tub}^\eta(\Gamma)$ and $\Gamma \times (-\eta, \eta)$. Since $g \in L^2(\Gamma)$, $\psi \in H^1(\Gamma)$ and $g^E \in L^2(\Omega)$, $\psi^E \in H^1(\Omega)$, by Lemma 5.18 we have,

$$\int_\Omega \delta_\varepsilon g^E \psi^E\, dx \to \int_\Gamma g\psi\, d\mathcal{H} \text{ as } \varepsilon \to 0. \tag{5.4.5}$$

By (5.2.17), we have

$$\|v^\varepsilon\|^2_{1,\delta_\varepsilon} \le \|(u^\varepsilon, v^\varepsilon)\|^2_{\mathcal{X}_\varepsilon} \le C(\left\|f^E\right\|^2_{L^2(\Omega)} + \left\|g^E\right\|^2_{L^2(\Omega)})$$

and so by the proof of Lemma 5.26, there exists a function $\tilde{v} \in H^1(\Gamma)$ such that, as $\varepsilon \to 0$,

$$\begin{aligned}\chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z) V^\varepsilon(p,z) &\rightharpoonup \tilde{v}(p) \text{ in } L^2(\Gamma \times \mathbb{R}, \delta), \\ \chi_{(\frac{-\eta}{\varepsilon^{1-k}}, \frac{\eta}{\varepsilon^{1-k}})}(z)(\nabla_\Gamma V^\varepsilon + \nabla^\Gamma_{\varepsilon z} V^\varepsilon)(p,z) &\rightharpoonup \nabla_\Gamma \tilde{v}(p) \text{ in } (L^2(\Gamma \times \mathbb{R}, \delta))^n.\end{aligned}$$

We see that, by the definition of b^E, (5.2.17), and Lemma 5.26 (with ψ^E replaced by $b^E\psi^E$),

$$\int_\Omega \delta_\varepsilon b^E v^\varepsilon \psi^E\, dx \to \int_\Gamma b\tilde{v}\psi\, d\mathcal{H} \text{ as } \varepsilon \to 0. \tag{5.4.6}$$

Similarly, by the definition of $\mathcal{B}^E$, (5.2.17), and Lemma 5.26 (with $\nabla\psi^E$ replaced by $(\mathcal{B}^E)^T\nabla\psi^E$,

$$\int_\Omega \delta_\varepsilon \mathcal{B}^E \nabla v^\varepsilon \cdot \nabla \psi^E\, dx \to \int_\Gamma \mathcal{B}\nabla_\Gamma \tilde{v} \cdot \nabla_\Gamma \psi\, d\mathcal{H} \text{ as } \varepsilon \to 0. \tag{5.4.7}$$

Hence, as $\varepsilon \to 0$,

$$\begin{aligned}&\int_\Omega \mathcal{B}^E \delta_\varepsilon \nabla v^\varepsilon \cdot \nabla \psi^E + b^E \delta_\varepsilon v^\varepsilon \psi^E - \beta\delta_\varepsilon g^E \psi^E + K\delta_\varepsilon v^\varepsilon(\psi^E - \varphi^E)\, dx \\ \to &\int_\Gamma \mathcal{B}\nabla_\Gamma \tilde{v} \cdot \nabla_\Gamma \psi + b\tilde{v}\psi - \beta g\psi + K\tilde{v}(\psi - \gamma_0(\varphi))\, d\mathcal{H}.\end{aligned}$$

Together with (5.4.4), we see that $(\tilde{u}, \tilde{v})$ satisfies the weak formulation of (CSI) with arbitrary $\varphi \in H^1(\Omega^{(1)})$ and $\psi \in H^1(\Gamma)$. Hence, $(\tilde{u}, \tilde{v})$ is a weak solution to (CSI) and by the well-posedness of (CSI) we have $\tilde{u} = u$ and $\tilde{v} = v$.

Next, we can choose $\varphi = u \in H^1(\Omega^{(1)})$ and $\psi = v \in H^1(\Gamma)$. Then the extensions u^E (via the Extension theorem) and v^E (as in the proof of Corollary 5.17) are admissible test functions in (5.2.12). Furthermore, by the coercivity of the bilinear form $a_{CDD}(\cdot, \cdot)$ and that $\xi \geq \frac{1}{2}$ in $\Omega^{(1)}$, we obtain

$$\begin{aligned}
&C(\theta_i, K)\Big(\|u^\varepsilon - u\|^2_{H^1(\Omega^{(1)})} + \|v^\varepsilon - v^E\|^2_{1,\delta_\varepsilon} \Big) \\
&\leq C(\theta_i, K)\Big(\|u^\varepsilon - u^E\|^2_{1,\xi_\varepsilon} + \|u^\varepsilon - u^E\|^2_{0,\delta_\varepsilon} + \|v^\varepsilon - v^E\|^2_{1,\delta_\varepsilon} \Big) \\
&\leq a_{CDD}((u^\varepsilon - u^E, v^\varepsilon - v^E), (u^\varepsilon - u^E, v^\varepsilon - v^E)) \\
&= l_{CDD}((u^\varepsilon - u^E, v^\varepsilon - v^E)) - a_{CDD}((u^E, v^E), (u^\varepsilon - u^E, v^\varepsilon - v^E)).
\end{aligned}$$

We observe that by (5.4.1) with φ^E replaced by u^E, (5.4.2) with $a^E\varphi^E$ replaced by f^E, (5.4.5) with ψ^E replaced by v^E, and (5.4.6) with $b^E\psi^E$ replaced by g^E,

$$l_{CDD}((u^\varepsilon - u^E, v^\varepsilon - v^E)) = \int_\Omega \xi_\varepsilon f^E(u^\varepsilon - u^E) + \beta\delta_\varepsilon g^E(v^\varepsilon - v^E)\, dx \to 0 \text{ as } \varepsilon \to 0.$$

Meanwhile, we have that

$$\begin{aligned}
&a_{CDD}((u^E, v^E), (u^\varepsilon - u^E, v^\varepsilon - v^E)) \\
&= \int_\Omega \xi_\varepsilon(\mathcal{A}^E\nabla u^E \cdot \nabla(u^\varepsilon - u^E) + a^E u^E(u^\varepsilon - u^E))\, dx \\
&+ \int_\Omega \delta_\varepsilon(\mathcal{B}^E\nabla v^E \cdot \nabla(v^\varepsilon - v^E) + b^E v^E(v^\varepsilon - v^E))\, dx \\
&+ \int_\Omega K\delta_\varepsilon(v^E - u^E)(v^\varepsilon - u^\varepsilon - v^E + u^E)\, dx.
\end{aligned}$$

Using (5.4.1) with $f^E\varphi^E$ replaced by $a^E\left|u^E\right|^2$ and $\mathcal{A}^E\nabla u^E \cdot \nabla u^E$, (5.4.3) with φ^E replaced by u^E, and (5.4.2) with φ^E replaced by u^E, the first term on the right hand side converges to zero as $\varepsilon \to 0$.

Similarly, by (5.3.21) with $\left|f^E\right|^2$ replaced by $b^E\left|v^E\right|^2$ and $\left|\nabla f^E\right|^2$ replaced by $\mathcal{B}^E\nabla v^E \cdot \nabla v^E$, (5.4.6) with ψ^E replaced by v^E, and (5.4.7) with ψ^E replaced by v^E, the second term on the right hand side converges to zero as $\varepsilon \to 0$.

In addition, by (5.3.32) with φ replaced by $K(v^E - u^E)$, (5.4.6) with $b^E\psi^E$ replaced by $K(v^E - u^E)$, and (5.3.24) with f replaced by $K\left|v^E - u^E\right|^2$, the third term on the right hand side also converge to zero as $\varepsilon \to 0$.

Thus,

$$\|u^\varepsilon - u\|^2_{H^1(\Omega^{(1)})} + \left\|u^\varepsilon - u^E\right\|^2_{0,\delta_\varepsilon} + \left\|v^\varepsilon - v^E\right\|^2_{1,\delta_\varepsilon} \to 0 \text{ as } \varepsilon \to 0,$$

and so u^ε converges strongly to u in $H^1(\Omega^{(1)})$. Meanwhile, by the triangle inequality and (5.3.21) with f^E replaced by v^E,

$$\begin{aligned}\left|\|v^\varepsilon\|_{1,\delta_\varepsilon} - \|v\|_{H^1(\Gamma)}\right| &\le \left|\|v_\varepsilon\|_{1,\delta_\varepsilon} - \left\|v^E\right\|_{1,\delta_\varepsilon}\right| + \left|\left\|v^E\right\|_{1,\delta_\varepsilon} - \|v\|_{H^1(\Gamma)}\right| \\ &\le \left\|v^\varepsilon - v^E\right\|_{1,\delta_\varepsilon} + \left|\left\|v^E\right\|_{1,\delta_\varepsilon} - \|v\|_{H^1(\Gamma)}\right| \to 0 \text{ as } \varepsilon \to 0.\end{aligned}$$

Hence, we obtain the norm convergence

$$\|v^\varepsilon\|_{1,\delta_\varepsilon} \to \|v\|_{H^1(\Gamma)} \text{ as } \varepsilon \to 0.$$

We remark that the analogous convergence of (SDD) to (SSI) is covered by the above analysis by setting $\mathcal{A}^E = a^E = K = f^E = 0$ and $\beta = 1$, while the analogous convergence of (NDDH) to (NSIH) is covered by setting $\mathcal{B}^E = b^E = K = g^E = 0$ and replacing f^E with $f^E + \nabla\cdot(\mathcal{A}^E\hat{g}^E) - a^E\hat{g}^E$. The convergence of (RDD) to (RSI) is covered by set $\mathcal{B}^E = b^E = 0$, $v^\varepsilon = v^E = 0$ and $K = \beta$.

For the convergence of (DDDH) to (DSIH), we extend $w_D \in H^1_0(\Omega^{(1)})$ to $w_D^E \in H^1_{\Gamma,0}(\Omega)$ by zero outside $\Omega^{(1)}$. Then, by Lemma 5.27, $w_D^E \in \mathcal{W}_\varepsilon$ is an admissible test function in (5.2.15). Following a similar argument to the analysis of (CDD), we have that

$$\begin{aligned}&C(\theta_0,\theta_2)\left\|w_D^\varepsilon - w_D^E\right\|^2_{H^1(\Omega^{(1)})} \\ \le\ &\int_\Omega \xi_\varepsilon(f^E - a^E\tilde{g}^E)(w_D^\varepsilon - w_D^E) + \xi_\varepsilon\mathcal{A}^E\nabla\tilde{g}^E\cdot\nabla(w_D^\varepsilon - w_D^E)\,dx \\ -\ &\int_\Omega \xi_\varepsilon(\mathcal{A}^E\nabla w_D^E\cdot\nabla(w_D^\varepsilon - w_D^E) + a^E w_D^E(w_D^\varepsilon - w_D^E)) + \frac{1}{\varepsilon}\delta_\varepsilon w_D^E(w_D^\varepsilon - w_D^E)\,dx.\end{aligned}$$

By arguing similarly as in the convergence analysis of (CDD), all the terms on the right hand side involving ξ_ε converge to zero as $\varepsilon \to 0$. Furthermore, by (5.3.54) and (5.2.20),

$$\begin{aligned}&\left|\int_\Omega \frac{1}{\varepsilon}\delta_\varepsilon w_D^E(w_D^\varepsilon - w_D^E)\,dx\right| \le \left\|w_D^E\right\|_{0,\frac{1}{\varepsilon}\delta_\varepsilon}\left(\|w_D^\varepsilon\|_{0,\frac{1}{\varepsilon}\delta_\varepsilon} + \left\|w_D^E\right\|_{0,\frac{1}{\varepsilon}\delta_\varepsilon}\right) \\ &\le C\left\|w_D^E\right\|_{0,\frac{1}{\varepsilon}\delta_\varepsilon}\left(\left\|f^E\right\|_{L^2(\Omega)} + \|\tilde{g}\|_{H^1(\Omega^{(1)})} + \|w_D\|_{H^1(\Omega^{(1)})}\right) \to 0 \text{ as } \varepsilon \to 0.\end{aligned}$$

Hence, we have

$$\left\|w_D^\varepsilon - w_D^E\right\|^2_{H^1(\Omega^{(1)})} \to 0 \text{ as } \varepsilon \to 0.$$

5.5 Numerical experiments

In this section, we report on numerical experiments that support the above analysis.

5.5.1 1D Numerics

We consider the domain $\Omega^{(1)} := (-2, 2)$ and the following elliptic equation

$$-u''(x) + u(x) = f(x) \text{ for } x \in (-2, 2) \tag{5.5.1}$$

with one of the following boundary conditions

- (Neumann) $u'(y) = 0$ for $y = \pm 2$;
- (Dirichlet) $u(y) = 0$ for $y = \pm 2$;
- (Robin) $u'(y) + \beta u(y) = \beta g(y)$ for $y = \pm 2$.

We choose f and g so that $u(x) = \sin(\pi x)$ is the solution for the Dirichlet problem, while $u(x) = \cos(\pi x)$ is the solution to the Neumann and Robin problem (for $\beta = 1$).

We choose $\Omega = (-5, 5)$, and the corresponding diffuse domain approximations will be

$$\begin{aligned}
(\xi_\varepsilon (u_N^\varepsilon)')' + \xi_\varepsilon u_N^\varepsilon &= \xi_\varepsilon f^E \text{ for Neumann problem,} \\
(\xi_\varepsilon (u_D^\varepsilon)')' + \xi_\varepsilon u_D^\varepsilon + \frac{1}{\varepsilon}\delta_\varepsilon u_D^\varepsilon &= \xi_\varepsilon f^E \text{ for Dirichlet problem,} \\
(\xi_\varepsilon (u_R^\varepsilon)')' + \xi_\varepsilon u_R^\varepsilon + \beta\delta_\varepsilon u_R^\varepsilon &= \xi_\varepsilon f^E + \beta\delta_\varepsilon g^E \text{ for Robin problem.}
\end{aligned}$$

The signed distance function to $\Gamma = \{-2, 2\}$ is

$$d(x) = |x| - 2,$$

so that $d(x) < 0$ for $x \in \Omega^{(1)}$. For discretisation we employ linear finite elements and the method of Elliott et al. [2011], with a similar setup to Section 4.2.1.

Let $\mathcal{T}_h$ denote a uniform subdivision of Ω consisting of subintervals with size h. Let N be the number of vertices with coordinates denoted by $\{x_1, \ldots, x_N\}$. Let $\mathcal{S}^h$ be the discrete finite-element space of piecewise linear elements defined as

in (4.2.6), and $\Pi^h : C^0([-1,1]) \to \mathcal{S}^h$ denote the interpolation operator defined as in (4.2.7), with $\{\chi_j\}_{j=1}^N$ denoting the set of standard basis function such that $\chi_j \in C^0([-1,1])$ and χ_j is a linear polynomial on each interval $[x_i, x_{i+1}]$ satisfying $\chi_j(x_i) = \delta_{ji}$ for all $i, j = 1, \ldots, N$.

Let $\mathcal{X}_h$ and $\mathcal{D}_h$ be defined as in (4.2.4) and (4.2.5), respectively. Then, for the Robin problem, we find the finite element function $u_h^\varepsilon \in \mathcal{S}^h$ such that $u_h^\varepsilon(x_j) = 0$ if $j \notin \mathcal{X}_h \cup \mathcal{D}_h$ and satisfies

$$\begin{aligned}&\int_\Omega \Pi^h(\xi_\varepsilon)(u_h^\varepsilon)'(\chi_j)' + \Pi^h(\xi_\varepsilon u_h^\varepsilon \chi_j) + \beta \Pi^h(\delta_\varepsilon u_h^\varepsilon \chi_j)\\ =& \int_\Omega \Pi^h(\xi_\varepsilon f^E \chi_j) + \beta \Pi^h(\delta_\varepsilon g^E \chi_j) \text{ for all } j = 1, \ldots, N.\end{aligned}$$

We obtain the method for the Neumann problem by setting $\beta \equiv 0$, while the method for the Dirichlet problem is obtained by setting $\beta = \varepsilon^{-1}$ and $g^E \equiv 0$. The above numerical method has been implemented using the software MATLAB, Version 7.8.0 (R2012b) MATLAB [2010] and we choose regularisations $\xi_\varepsilon, \delta_\varepsilon$ originating from the double-well potential (see (5.2.9)).

For fixed h, ε, we denote $e(h, \varepsilon)$ as the error under consideration and the experimental order of convergence is defined as

$$\text{e.o.c} = \log(e(mh, m\varepsilon)/e(h, \varepsilon))/\log(m),$$

where m is the rate as which we decrease the mesh size.

We choose $\varepsilon = 4h$ to allow for 4 elements in the interfacial region. The results are displayed in Tables 5.1, 5.2 and 5.3 for the Neumann, Robin and Dirichlet problems, respectively. For both the Neumann and Robin problems, we observe quadratic convergence for the L^2-error and linear convergence for the gradient error, while for the Dirichlet problem, we observe linear and sublinear convergence for the L^2-error and the gradient error, respectively. Although our analysis does not indicate a rate of convergence based on ε, we expected the order of convergence of the L^2-error for the Dirichlet problem should be at least one order lower than that of the Robin problem, as β is set to be $\frac{1}{\varepsilon}$ (see also (5.3.26) with $q = 2$). The order of convergence in the gradient is not affected as β is not present in any higher order terms.

We remark that in one dimension, by Theorem 5.14 and the Sobolev embedding theorem $H^1 \hookrightarrow L^\infty$, we have that

$$\|u^\varepsilon - u\|_{L^\infty((-2,2))} \to 0 \text{ as } \varepsilon \to 0,$$

for all three problems. Tables 5.1, and 5.2 suggest cubic convergence for $\|u^\varepsilon - u\|_{L^\infty((-2,2))}$ and quadratic convergence for $\|\nabla(u^\varepsilon - u)\|_{L^\infty((-2,2))}$ for the Neumann and Robin problems, while Table 5.3 suggests quadratic and linear convergence for $\|u^\varepsilon - u\|_{L^\infty((-2,2))}$ and $\|\nabla(u^\varepsilon - u)\|_{L^\infty((-2,2))}$, respectively.

However, since we do not have any theoretical results on the rate of convergence in ε, we cannot directly compare our results with the results of Franz et al. [2012]. Moreover, the setting of Franz et al. [2012] considers diffuse domain approximations that extends only one side of the boundary, for instance the point $x = -2$. Thus, their setting is different from the setting we consider in this chapter.

h	$\|u - u^\varepsilon\|_{L^2}$	E.O.C	$\|u - u^\varepsilon\|_{L^\infty}$	E.O.C
0.1	0.180446887	-	0.02537938	-
0.05	0.063847740	1.49886	0.00682904	1.89390
0.025	0.014806448	2.10841	0.00114060	2.58189
0.0125	0.002902885	2.35067	1.590151×10^{-4}	2.84255
0.00625	5.355734×10^{-4}	2.43833	2.077546×10^{-5}	2.93621
0.003125	9.665788×10^{-5}	2.47012	2.647726×10^{-6}	2.97205
h	$\|\nabla(u - u^\varepsilon)\|_{L^2}$	E.O.C	$\|\nabla(u - u^\varepsilon)\|_{L^\infty}$	E.O.C
0.1	1.07988807	-	0.18401017	-
0.05	0.58008470	0.89655	0.06305146	1.54518
0.025	0.25779875	1.17002	0.01744371	1.85382
0.0125	0.11176024	1.20584	0.00448237	1.96037
0.00625	0.05025375	1.15310	0.00112852	1.98983
0.003125	0.02353528	1.09441	0.00028263	1.99743

Table 5.1: h, ε-convergence table for Neumann problem, $\varepsilon = 4h$, $\Omega := (-5, 5)$.

h	$\|u - u^\varepsilon\|_{L^2}$	E.O.C	$\|u - u^\varepsilon\|_{L^\infty}$	E.O.C
0.1	0.28501476	-	0.02879628	-
0.05	0.11652669	1.29038	0.00589959	2.28719
0.025	0.03442458	1.75915	9.238317×10^{-4}	2.67491
0.0125	0.00908349	1.92212	1.287579×10^{-4}	2.84297
0.00625	0.00231319	1.97336	1.703813×10^{-5}	2.91782
0.003125	5.823455×10^{-4}	1.98994	2.198770×10^{-6}	2.95399
h	$\|\nabla(u - u^\varepsilon)\|_{L^2}$	E.O.C	$\|\nabla(u - u^\varepsilon)\|_{L^\infty}$	E.O.C
0.1	1.25494421	-	0.25173594	-
0.05	0.63908688	0.97353	0.08705289	1.53195
0.025	0.28284729	1.17599	0.02496885	1.80176
0.0125	0.12123098	1.22226	0.00660473	1.91856
0.00625	0.05330553	1.18540	0.00169205	1.96473
0.003125	0.02441650	1.12643	4.277776×10^{-4}	1.98384

Table 5.2: h, ε-convergence table for Robin problem, $\varepsilon = 4h$, $\Omega := (-5, 5)$.

h	$\|u-u^\varepsilon\|_{L^2}$	E.O.C	$\|u-u^\varepsilon\|_{L^\infty}$	E.O.C
0.1	0.43855097	-	0.05494411	-
0.05	0.36770267	0.25420	0.02128475	1.36814
0.025	0.22783636	0.69054	0.00632594	1.75047
0.0125	0.12364193	0.88183	0.00169331	1.90144
0.00625	0.06387014	0.95295	0.00043570	1.95842
0.003125	0.03238435	0.97984	0.00011035	1.98127
h	$\|\nabla(u-u^\varepsilon)\|_{L^2}$	E.O.C	$\|\nabla(u-u^\varepsilon)\|_{L^\infty}$	E.O.C
0.1	1.01951657	-	0.10300934	-
0.05	0.64264593	0.66579	0.05009439	1.36814
0.025	0.37058587	0.79422	0.02207178	1.18245
0.0125	0.21022915	0.81784	0.00990959	1.15530
0.00625	0.12282882	0.77531	0.00463239	1.09707
0.003125	0.07538918	0.70422	0.00223138	1.05382

Table 5.3: h, ε-convergence table for Dirichlet problem, $\varepsilon = 4h$, $\Omega := (-5, 5)$.

5.5.2 2D Numerics

In two dimensions, we consider the coupled bulk-surface system:

$$\begin{aligned} -\Delta u + u &= f, \text{ in } B(0,1), \\ -\Delta_\Gamma v + v + \nabla u \cdot \nu &= g, \text{ on } S^1, \\ \nabla u \cdot \nu &= (v - u), \text{ on } S^1. \end{aligned}$$

We choose

$$f(x,y) = \frac{y}{2}, \quad g(x,y) = 4y - 2y^3 - 2yx^2 + \frac{y}{2},$$

so that the exact solution is

$$u(x,y) = \frac{y}{2} \text{ in } B(0,1), \quad v(x,y) = y \text{ on } S^1,$$

and

$$\|v\|^2_{L^2(\Gamma)} = \|\nabla_\Gamma v\|^2_{L^2(\Gamma)} = \pi.$$

We choose Ω to be the square $(-2,2)^2$ and let $\mathcal{T}_h$ denote a triangulation of Ω consisting of simplices with maximal diameter $h = \max_{e \in \mathcal{T}_h} \operatorname{diam}(e)$. Let N be the number of vertices with coordinates denoted by $\{\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N\}$ and let $\mathcal{S}^h$ denote

the discrete finite element space:

$$\mathcal{S}^h := \{v_h \in C^0(\overline{\Omega}) : v_h|_e \in P^1(e) \text{ for each } e \in \mathcal{T}_h\}.$$

We seek finite element functions $u_h^\varepsilon, v_h^\varepsilon \in \mathcal{S}^h$ such that

$$\int_\Omega \Pi^h(\xi_\varepsilon)\nabla u_h^\varepsilon \cdot \nabla\varphi + \Pi^h(\xi_\varepsilon u_h^\varepsilon\varphi) - \Pi^h(\delta_\varepsilon(v_h^\varepsilon - u_h^\varepsilon)\varphi)\,dx = \int_\Omega \Pi^h(\xi_\varepsilon f^E\varphi)\,dx,$$
$$\int_\Omega \Pi^h(\delta_\varepsilon)\nabla v_h^\varepsilon \cdot \nabla\psi + \Pi^h(\delta_\varepsilon v_h^\varepsilon\psi) + \Pi^h(\delta_\varepsilon(v_h^\varepsilon - u_h^\varepsilon)\psi)\,dx = \int_\Omega \Pi^h(\delta_\varepsilon g^E\psi)\,dx,$$

for all $\varphi, \psi \in \mathcal{S}^h$. Let $\{\chi_1, \ldots, \chi_N\}$ denote the standard basis functions of $\mathcal{S}^h$ and we define, for $1 \le i, j \le N$,

$$M_{ij}^\xi := \int_\Omega \Pi^h(\xi_\varepsilon\chi_i\chi_j), \quad A_{ij}^\xi := \int_\Omega \Pi^h(\xi_\varepsilon)\nabla\chi_i \cdot \nabla\chi_j,$$

with $M_{ij}^\delta, A_{ij}^\delta$ defined similarly. Then, our discrete scheme is equivalent to solving

$$\begin{pmatrix} A^\xi + M^\xi + M^\delta & -KM^\delta \\ -M^\delta & A^\delta + 2M^\delta \end{pmatrix} \begin{pmatrix} \boldsymbol{u} \\ \boldsymbol{v} \end{pmatrix} = \begin{pmatrix} \boldsymbol{F} \\ \boldsymbol{G} \end{pmatrix},$$

where

$$\boldsymbol{u} = (u_1, \ldots, u_N)^T, \quad (\boldsymbol{F})_i = \int_\Omega \Pi^h(\xi_\varepsilon f^E\chi_i)\,dx,$$

and $\boldsymbol{v}, \boldsymbol{G}$ are defined similarly.

In the implementation, we used the double-obstacle versions for ξ_ε and δ_ε (see (5.2.10)). We choose $\varepsilon = 2h$, which allows for 8 elements in the interfacial layer (see Figure 5.1). We observe from Figure 5.1 the finite element approximations of the bulk and surface solutions at the finest level $h = 0.05/\sqrt{2}$ and they are in good agreement with the true solutions. In particular, the double-obstacle regularisation generates an interfacial region around S^1 and the finite element function v_h^ε is zero outside the interfacial region.

In Table 5.4, we observe the strong convergence for the bulk quantity in $H^1(\Omega^{(1)})$ and the norm convergence for the surface quantity, as indicated by Theorem 5.14. In particular, we see quadratic convergence for the bulk L^2-error and linear convergence for the bulk gradient error, which is expected from standard finite element theory. For the norm convergence of the surface quantity, we obtain quadratic convergence for both the L^2-norm and the gradient norm.

We also perform numerical experiments for a bulk elliptic equation with

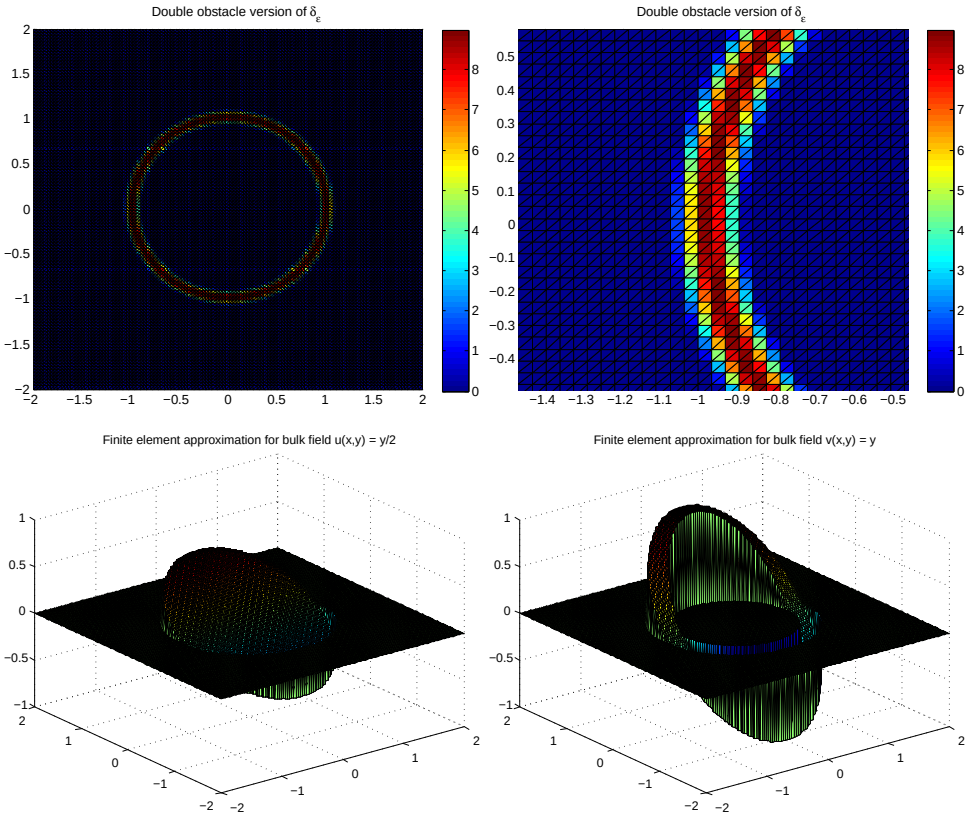


Figure 5.1: (Top) Double-obstacle regularisation δ_ε. (Bottom) Finite element approximations of the bulk and surface solution at $h = 0.05/\sqrt{2}$ and $\varepsilon = 2h$

h	$\|u - u^\varepsilon\|_{L^2(\Omega^{(1)})}$	E.O.C	$\|\nabla(u - u^\varepsilon)\|_{L^2(\Omega^{(1)})}$	E.O.C
0.2	0.085836794	-	0.196641003	-
$0.2/\sqrt{2}$	0.037089715	2.42115	0.096933568	2.04099
0.1	0.018032476	2.08084	0.063101193	1.23866
$0.1/\sqrt{2}$	0.008635846	2.12438	0.037640663	1.49075
0.05	0.004276931	2.43833	0.028165375	0.83674
$0.05/\sqrt{2}$	0.002163992	1.96576	0.019818221	1.01419
h	$\|v\|_{L^2(\Gamma)} - \|v^\varepsilon\|_{0,\delta_\varepsilon}$	E.O.C	$\|\nabla_\Gamma v\|_{L^2(\Gamma)} - \|\nabla v^\varepsilon\|_{0,\delta_\varepsilon}$	E.O.C
0.2	0.322784855	-	0.266489117	-
$0.2/\sqrt{2}$	0.163953203	1.95458	0.135869920	1.94370
0.1	0.079966163	2.07165	0.065947462	2.08567
$0.1/\sqrt{2}$	0.040530189	1.96079	0.033243411	1.97680
0.05	0.019590159	2.09774	0.015987812	2.11219
$0.05/\sqrt{2}$	0.009769039	2.00768	0.007933911	2.02174

Table 5.4: h, ε-convergence table for coupled bulk-surface problem, $\varepsilon = 2h$, $\Omega := [-2, 2]^2$. We note that $\|v^\varepsilon\|_{0,\delta_\varepsilon} < \|v\|_{L^2(\Gamma)}$, $\|\nabla v^\varepsilon\|_{0,\delta_\varepsilon} < \|\nabla_\Gamma v\|_{L^2(\Gamma)}$.

Neumann, Robin and Dirichlet boundary conditions. We consider

$$-\Delta u + u = f \text{ in } B(0,1),$$

with

- (Neumann) $\nabla u \cdot \nu = 0$ on S^1,
- (Robin) $\nabla u \cdot \nu + u = g$ on S^1,
- (Dirichlet) $u = 0$ on S^1.

We choose f, g so that the true solutions are

$$u(x,y) = \sin\left(\frac{\pi}{2}(x^2+y^2)\right) \text{ for Neumann and Robin,}$$
$$u(x,y) = \cos\left(\frac{\pi}{2}(x^2+y^2)\right) \text{ for Dirichlet.}$$

The diffuse domain approximations are similar to those in Section 5.5.1. For the implementation we use the double obstacle regularisation and solve for $\boldsymbol{u}_N, \boldsymbol{u}_R, \boldsymbol{u}_D \in \mathcal{S}^h$ such that

$$(A^\xi + M^\xi)\boldsymbol{u}_N = \boldsymbol{F},$$
$$(A^\xi + M^\xi + M^\delta)\boldsymbol{u}_R = \boldsymbol{F},$$
$$(A^\xi + M^\xi + \tfrac{1}{\varepsilon}M^\delta)\boldsymbol{u}_D = \boldsymbol{F}.$$

The results are shown in Table 5.5 and we observe quadratic convergence for the L^2-error and linear convergence for gradient error for both the Neumann and Robin problems. While for the Dirichlet problem, we observe linear convergence for both the L^2-error and the gradient error.

h	$\|u-u_N^\varepsilon\|_{L^2(\Omega^{(1)})}$	E.O.C	$\|\nabla(u-u_N^\varepsilon)\|_{L^2(\Omega^{(1)})}$	E.O.C
0.2	1.76872642	-	2.09553368	-
$0.2/\sqrt{2}$	0.86581225	2.06116	1.03796492	2.02712
0.1	0.43797992	1.96638	0.66840583	1.26992
$0.1/\sqrt{2}$	0.21850510	2.00639	0.36880279	1.71575
0.05	0.05369359	2.10442	0.21998325	1.49091
$0.05/\sqrt{2}$	0.05154458	2.06313	0.12543014	1.62102
h	$\|u-u_R^\varepsilon\|_{L^2(\Omega^{(1)})}$	E.O.C	$\|\nabla(u-u_R^\varepsilon)\|_{L^2(\Omega^{(1)})}$	E.O.C
0.2	0.25862942	-	0.91343663	-
$0.2/\sqrt{2}$	0.11614562	2.30990	0.49019011	1.79593
0.1	0.05676312	2.0658	0.32116654	1.22004
$0.1/\sqrt{2}$	0.02768839	2.07135	0.19895948	1.38169
0.05	0.01274990	2.2376	0.12989706	1.23021
$0.05/\sqrt{2}$	0.00572483	2.31036	0.08572989	1.19899
h	$\|u-u_D^\varepsilon\|_{L^2(\Omega^{(1)})}$	E.O.C	$\|\nabla(u-u_D^\varepsilon)\|_{L^2(\Omega^{(1)})}$	E.O.C
0.2	0.61076826	-	2.71992769	-
$0.2/\sqrt{2}$	0.36210464	1.50844	1.52685839	1.01691
0.1	0.26790779	0.86888	1.49745890	0.05609
$0.1/\sqrt{2}$	0.17701347	1.19622	1.14506950	0.77416
0.05	0.12282312	1.05455	0.97949266	0.45066
$0.05/\sqrt{2}$	0.08557115	1.04277	0.73744070	0.81902

Table 5.5: h, ε-convergence table for 2D Neumann, Robin and Dirichlet problems, $\varepsilon = h$, $\Omega := (-2, 2)^2$.

Appendix A

Evolving surfaces and transport identities

This chapter contains a list of important results regarding evolving surfaces and transport identities. The main results in this chapter are taken from Cermelli, Fried, and Gurtin [2005] and Chapter 5 of Dziuk and Elliott [2013]. Let $T > 0$ be fixed.

Theorem A.1 (Reynold's transport theorem)**.** *Let $R(t)$ denote a time-dependent region of $\mathbb{R}^n$ where the boundary $\partial R(t)$ moves with velocity $\boldsymbol{v}$. Let $\Phi(x,t)$ denote a bulk scalar field defined over $R(t)$. Then*

$$\frac{d}{dt}\int_{R(t)} \Phi(x,t) = \int_{R(t)} \frac{\partial \Phi}{\partial t} + \nabla \cdot (\Phi \boldsymbol{v}).$$

Definition A.2 (Material derivative for bulk quantities)**.** Given a scalar field $\Phi(x,t)$ defined in a time-dependent region $R(t)$ moving with velocity field $\boldsymbol{v}$. We define its material derivative $\partial_t^\bullet \Phi(x,t)$ to be

$$\partial_t^\bullet \Phi(x,t) := \frac{\partial \Phi}{\partial t}(x,t) + \nabla \Phi(x,t) \cdot \boldsymbol{v}(x,t).$$

Definition A.3 (Evolving hypersurface)**.** We call $\Gamma \subset \mathbb{R}^{n+1}$ a C^2 compact evolving hypersurface if, for each $t \in [0,T]$, there exists a compact hypersurface $\Gamma(t) \subset \mathbb{R}^n$ oriented by a normal vector field $\boldsymbol{\nu}(\cdot,t)$ and a diffeomorphism $G(\cdot,t) : \Gamma(0) \to \Gamma(t)$ with $G \in C^1([0,T], C^2(\Gamma(0)))$ such that

$$\Gamma = \bigcup_{t\in[0,T]} \Gamma(t) \times \{t\}.$$

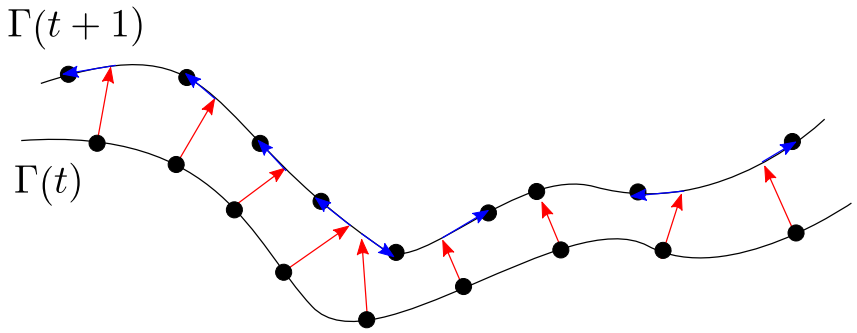


Figure A.1: The normal velocity, indicated in red, describes the evolution of the surface, while the tangential velocity, indicated in blue, describes the evolution of material points along the surface.

The evolution of $\Gamma(t)$ is encoded by the velocity field $\boldsymbol{v}(\cdot, t)$, which satisfies

$$\boldsymbol{v}(G(\cdot,t),t) = \frac{\partial G}{\partial t}(\cdot,t), \quad G(\cdot,0) = \mathrm{Id}. \tag{A.0.1}$$

This velocity field can be decomposed into a normal component $\boldsymbol{v}_\nu := (\boldsymbol{v}\cdot\boldsymbol{\nu})\boldsymbol{\nu}$ and a tangential component $\boldsymbol{v}_\tau$. The normal velocity $\boldsymbol{v}_\nu$ is sufficient to describe the geometric evolution of the hypersurface. A tangential velocity is needed when we consider surface quantities transported by the evolution of the hypersurface.

From Figure A.1 we observe that a material point $x \in \Gamma(t)$ need not lie in $\Gamma(t+1)$. Hence, the conventional time and spatial derivative $\partial_t(\cdot)$ and $\nabla(\cdot)$ for a surface scalar field φ may not be well-defined at an arbitrary point x. It is natural to consider a time derivative that follows the evolution of $\Gamma(t)$. The simplest such time derivative makes use of (A.0.1) and may be defined as follows:

Definition A.4 (Material derivative for surface quantities)**.** Given a scalar field φ defined on an evolving hypersurface Γ with associated velocity field $\boldsymbol{v}$. We define its material derivative $\partial_t^\bullet \varphi$ by

$$\partial_t^\bullet \varphi(x,t) := \frac{d}{ds}\varphi(G(x_0,s),s)\Big|_{s=t},$$

where x_0 is a point such that $G(x_0,t) = x$.

For each $t \in [0,T]$, we denote by $\mathcal{N}(t) \subset \mathbb{R}^n$ an open neighbourhood of $\Gamma(t)$ and set

$$\mathcal{N} := \bigcup_{[0,T]} \mathcal{N}(t) \times \{t\}.$$

Suppose φ can be smoothly extended from Γ to a function $\tilde{\varphi}$ defined on $\mathcal{N}$. Then by the chain rule, we obtain another definition of the material derivative for a surface scalar field:

$$\partial_t^\bullet \varphi(x,t) = \frac{d}{ds}\tilde{\varphi}(G(x_0,s),s)\Big|_{s=t} = \frac{\partial \tilde{\varphi}}{\partial t}(x,t) + \boldsymbol{v}(x,t)\cdot\nabla\tilde{\varphi}(x,t).$$

Definition A.5 (Normal time derivative for surface quantities)**.** Given a scalar field φ defined on an evolving hypersurface Γ with associated velocity field $\boldsymbol{v}$ with normal component $\boldsymbol{v}_\nu$. We define its normal time derivative $\partial_t^\circ \varphi$ by

$$\partial_t^\circ \varphi := \frac{\partial \tilde{\varphi}}{\partial t} + \boldsymbol{v}_\nu \cdot \nabla\tilde{\varphi},$$

where $\tilde{\varphi}$ is any smooth extension of φ to $\mathcal{N}$.

Theorem A.6 (surface transport theorem - Theorem 5.1 of [Dziuk and Elliott, 2013])**.** *Let Γ be an evolving hypersurface with velocity field $\boldsymbol{v}$. For $t \in [0,T]$, let $\mathcal{M}(t)$ be an arbitrary subset of $\Gamma(t)$. Assume that f is a function such that all the following quantities exist. Then*

$$\frac{d}{dt}\int_{\mathcal{M}(t)} f \, d\mathcal{H} = \int_{\mathcal{M}(t)} \partial_t^\bullet f + f\nabla_{\Gamma(t)}\cdot \boldsymbol{v} \, d\mathcal{H}.$$

We state two useful results regarding integration over hypersurfaces. We remark that $d\mathcal{H}$ in connection with an integral over Γ denotes the $n-1$ dimensional Hausdorff measure and $d\mathcal{H}$ in connection with an integral over $\partial\Gamma$ denotes the $n-2$ dimensional Hausdorff measure.

Theorem A.7 (surface integration by parts - Theorem 2.10 of [Dziuk and Elliott, 2013])**.** *Assume Γ is a hypersurface in $\mathbb{R}^n$ with smooth boundary $\partial\Gamma$. Let $\boldsymbol{\nu}$, $\boldsymbol{\mu}$ and κ denote the unit normal, the external unit co-normal and the mean curvature of Γ, respectively. Then, for $f \in C^1(\overline{\Gamma})$,*

$$\int_\Gamma \nabla_\Gamma f \, d\mathcal{H} = \int_\Gamma f\kappa\boldsymbol{\nu} \, d\mathcal{H} + \int_{\partial\Gamma} f\boldsymbol{\mu} \, d\mathcal{H}.$$

Theorem A.8 (surface divergence theorem - Theorem 2.14 of [Dziuk and Elliott, 2013])**.** *Assume Γ is a hypersurface in $\mathbb{R}^n$ with smooth boundary $\partial\Gamma$. Let $\boldsymbol{\nu}$ and $\boldsymbol{\mu}$ denote the unit normal and the external unit co-normal of Γ, respectively. Then, for $f \in C^1(\overline{\Gamma}), g \in C^2(\overline{\Gamma})$,*

$$\int_\Gamma \nabla_\Gamma f \cdot \nabla_\Gamma g \, d\mathcal{H} = -\int_\Gamma f\Delta_\Gamma g \, d\mathcal{H} + \int_{\partial\Gamma} f\nabla_\Gamma g \cdot \boldsymbol{\mu} \, d\mathcal{H}.$$

Appendix B

Equivalent distributional forms for the surfactant equations

We use the following result from Alt [2009] to reformulate the strong form of the surfactant equations (2.3.4), (2.3.7), (2.3.8) into an equivalent distributional form. Let $\mathcal{D}'(\Omega)$ denote the space of distributions on Ω.

Theorem B.1 (c.f. [Alt, 2009] Section 2.7 & Theorem 2.8)**.** *Given an open set $D \subset \mathbb{R}\times\mathbb{R}^d$ consisting of two open sets $\Omega^{(1)}$ and $\Omega^{(2)}$ separated by a smooth evolving hypersurface Γ, in particular, $\Gamma \subset D$ has no boundary within D. For $(t,x) \in \Gamma$ we let $\boldsymbol{\nu}_i(t,x) \in (T_x(\Gamma(t)))^\perp \subset \mathbb{R}^d$ be the external unit normal of $\Omega^{(i)}(t)$. Then $\boldsymbol{\nu}_1+\boldsymbol{\nu}_2 = \mathbf{0}$. Denote by $\chi_{\Omega^{(1)}}, \chi_{\Omega^{(2)}}, \delta_\Gamma$ the following distributions:*

$$\int_D f d\chi_{\Omega^{(i)}} = \int_{\mathbb{R}} \int_{\Omega^{(i)}(t)} f(t,x), \quad \int_D f d\delta_\Gamma = \int_{\mathbb{R}} \int_{\Gamma(t)} f(t,x). \tag{B.0.1}$$

A single balance law is an equality of the form

$$\partial_t E + \nabla \cdot \boldsymbol{Q} = F \text{ in } \mathcal{D}'(D) \tag{B.0.2}$$

with distributions given by

$$E = \sum_{i=1,2} e^{(i)} \chi_{\Omega^{(i)}} + e^\Gamma \delta_\Gamma,\ \boldsymbol{Q} = \sum_{i=1,2} \boldsymbol{q}^{(i)} \chi_{\Omega^{(i)}} + \boldsymbol{q}^\Gamma \delta_\Gamma,\ F = \sum_{i=1,2} f^{(i)} \chi_{\Omega^{(i)}} + f^\Gamma \delta_\Gamma,$$

where $e^{(i)}, q_j^{(i)}, f^{(i)} : \overline{\Omega^{(i)}} \to \mathbb{R}$ and $e^\Gamma, q_j^\Gamma, f^\Gamma : \Gamma \to \mathbb{R}$ are smooth functions. Then the distributional law $(B.0.2)$ is equivalent to the following:

1. *For* $i = 1, 2$ *in* $\Omega^{(i)}$

$$\partial_t e^{(i)} + \nabla \cdot \boldsymbol{q}^{(i)} = f^{(i)}.$$

2. *For all* $(t, x) \in \Gamma$

$$(\boldsymbol{q}^\Gamma - e^\Gamma \boldsymbol{u}_\Gamma)(t, x) \in T_x(\Gamma(t)).$$

3. *On* Γ

$$\partial_t e^\Gamma + \boldsymbol{u}_\Gamma \cdot \nabla e^\Gamma - e^\Gamma \boldsymbol{\kappa}_\Gamma \cdot \boldsymbol{u}_\Gamma + \nabla_\Gamma \cdot (\boldsymbol{q}^\Gamma - e^\Gamma \boldsymbol{u}_\Gamma) = f^\Gamma + \sum_{i=1,2} (\boldsymbol{q}^{(i)} - e^{(i)} \boldsymbol{u}_\Gamma) \cdot \boldsymbol{\nu}_i,$$

where $\boldsymbol{u}_\Gamma$ *is the unique velocity vector such that*

$$T_{(t,x)}\Gamma = span\{(1, \boldsymbol{u}_\Gamma(t, x))\} \oplus (\{0\} \times T_x\Gamma(t)),$$

and $\boldsymbol{\kappa}_\Gamma$ *is the curvature vector defined by*

$$\nabla_\Gamma \cdot \boldsymbol{n} = -\boldsymbol{\kappa}_\Gamma \cdot \boldsymbol{n},$$

for spatial normal vector fields $\boldsymbol{n}(t, x) \in (T_x\Gamma(t))^\perp$.

For the reformulation, we assume as in Teigen et al. [2009] that c^Γ is extended off Γ constant in the normal direction, hence $\nabla_\Gamma c^\Gamma = \nabla c^\Gamma$. Define

$$j_1 = \frac{1}{\alpha^{(1)}}(\gamma'(c^\Gamma) - G_1'(c^{(1)})), \quad j_2 = \frac{1}{\alpha^{(2)}}(\gamma'(c^\Gamma) - G_2'(c^{(2)})),$$

then by the definition of $\partial_t^\bullet(\cdot)$, the divergence-free property of $\boldsymbol{v}$ and that $\nabla\gamma'(c^\Gamma) = \gamma''(c^\Gamma)\nabla c = \gamma''(c^\Gamma)\nabla_\Gamma c^\Gamma = \nabla_\Gamma\gamma'(c^\Gamma)$, equation (2.3.7) can be written as

$$\partial_t c^\Gamma + \nabla_\Gamma \cdot (c^\Gamma \boldsymbol{v} - M_\Gamma \nabla\gamma'(c^\Gamma)) = -(j_1 + j_2).$$

Choosing $e^{(i)} = \boldsymbol{q}_j^{(i)} = f^{(i)} = 0$ for $i = 1, 2$, $1 \le j \le d$ and $e^\Gamma = c^\Gamma$, $\boldsymbol{q}^\Gamma = c^\Gamma \boldsymbol{v} - M_\Gamma \nabla\gamma'(c^\Gamma)$, $f^\Gamma = -(j_1 + j_2)$. Theorem B.1 implies that the distributional form

$$\partial_t(\delta_\Gamma c^\Gamma) + \nabla \cdot (\delta_\Gamma c^\Gamma \boldsymbol{v} - M_\Gamma \delta_\Gamma \nabla\gamma'(c^\Gamma)) = -\delta_\Gamma(j_1 + j_2) \tag{B.0.3}$$

is equivalent to

$$\partial_t c^\Gamma + \boldsymbol{u}_\Gamma \cdot \nabla c^\Gamma - c^\Gamma \boldsymbol{\kappa}_\Gamma \cdot \boldsymbol{u}_\Gamma + \nabla_\Gamma \cdot (c^\Gamma \boldsymbol{v} - M_\Gamma \nabla_\Gamma \gamma'(c^\Gamma) - c^\Gamma \boldsymbol{u}_\Gamma) = -(j_1 + j_2) \text{ on } \Gamma.$$

We have $\nabla_\Gamma \cdot (c^\Gamma \boldsymbol{u}_\Gamma) = -c^\Gamma \boldsymbol{\kappa}_\Gamma \cdot \boldsymbol{u}_\Gamma$ and $\boldsymbol{u}_\Gamma = (\boldsymbol{v} \cdot \boldsymbol{\nu}_1)\boldsymbol{\nu}_1$ implies $\boldsymbol{v} = \boldsymbol{u}_\Gamma + \boldsymbol{v}_\tau$. Furthermore, $\nabla_\Gamma \cdot (c^\Gamma \boldsymbol{v}) = \nabla_\Gamma c^\Gamma \cdot \boldsymbol{v}_\tau + c^\Gamma \nabla_\Gamma \cdot \boldsymbol{v}$. Hence equation (2.4.4) is equivalent to (2.3.7). For $i = 1$, choose $e^{(2)} = q_j^{(2)} = f^{(1)} = f^{(2)} = e^\Gamma = q_j^\Gamma = 0$ for $1 \le j \le d$ and $e^{(1)} = c^{(1)}$, $f^\Gamma = j_1$, and $\boldsymbol{q}^{(1)} = c^{(1)}\boldsymbol{v} - M_c^{(1)} \nabla G_1'(c^{(1)})$. Then the distributional form

$$\partial_t(\chi_{\Omega^{(1)}} c^{(1)}) + \nabla \cdot (\chi_{\Omega^{(1)}} c^{(1)} \boldsymbol{v} - \chi_{\Omega^{(1)}} M_c^{(1)} \nabla G_1'(c^{(1)})) = \delta_\Gamma j_1 \tag{B.0.4}$$

is equivalent to

$$\begin{aligned} \partial_t(c^{(1)}) + \nabla \cdot (c^{(1)}\boldsymbol{v} - M_c^{(1)} \nabla G_1'(c^{(1)})) = 0, \text{ in } \Omega^{(1)}, \\ M_c^{(1)} \nabla G_1'(c^{(1)}) \cdot \boldsymbol{\nu}_1 = j_1, \text{ on } \Gamma. \end{aligned}$$

Similarly, choosing $e^{(1)} = q_j^{(1)} = f^{(1)} = f^{(2)} = e^\Gamma = q_j^\Gamma = 0$ for $1 \le j \le d$ and $e^{(2)} = c^{(2)}$, $f^\Gamma = j_2$, and $\boldsymbol{q}^{(2)} = c^{(2)}\boldsymbol{v} - M_c^{(2)} \nabla G_2'(c^{(2)})$, then the distributional form

$$\partial_t(\chi_{\Omega^{(2)}} c^{(2)}) + \nabla \cdot (\chi_{\Omega^{(2)}} c^{(1)} \boldsymbol{v} - \chi_{\Omega^{(2)}} M_c^{(2)} \nabla G_2'(c^{(2)})) = \delta_\Gamma j_2 \tag{B.0.5}$$

is equivalent to

$$\begin{aligned} \partial_t(c^{(2)}) + \nabla \cdot (c^{(2)}\boldsymbol{v} - M_c^{(2)} \nabla G_2'(c^{(2)})) = 0, \text{ in } \Omega^{(2)}, \\ -M_c^{(2)} \nabla G_2'(c^{(2)}) \cdot \boldsymbol{\nu}_1 = j_2, \text{ on } \Gamma, \end{aligned}$$

as $\boldsymbol{\nu}_2 = -\boldsymbol{\nu}_1$. Thus the bulk and interfacial surfactant equations can be reformulated into the distributional forms $(B.0.3) - (B.0.5)$.

Appendix C

Functional analytical results

This chapter contains a list of important functional analytical and measure theoretical results used in Chapter 5.

Theorem C.1 (General Lebesgue dominated convergence, c.f. [Alt, 1999], pg. 52, Theorem. 1.21)**.** *Consider a set $D \subset \mathbb{R}^d$ and $p \in [1, \infty)$. For $k \in \mathbb{N}$, let $g_k \to g$ in $L^1(D; \mathbb{R})$ as $k \to \infty$ and let $f_k, f : D \to Y$ be measurable functions mapping into some Banach space Y such that*

(i) $f_k \to f$ almost everywhere as $k \to \infty$,

(ii) $|f_k|^p \leq g_k$ almost everywhere for all k.

Then $f_k, f \in L^p(D; Y)$ and

$$f_k \to f \text{ in } L^p(D; Y) \text{ as } k \to \infty.$$

Theorem C.2 (Extension theorem, c.f. [Evans, 1998], pg. 254, Theorem 1)**.** *Let $1 \leq p \leq \infty$ and let $D \subset \mathbb{R}^d$ be a bounded, open domain with C^1 boundary. Select a bounded open set U such that $D \subset\subset U$. Then there exists a bounded linear operator*

$$E : W^{1,p}(D) \to W^{1,p}(\mathbb{R}^d)$$

such that for each $u \in W^{1,p}(D)$:

(i) $Eu = u$ almost everywhere in D,

(ii) Eu has support within U,

(iii) $\|Eu\|_{W^{1,p}(\mathbb{R}^d)} \leq C_{ext} \|u\|_{W^{1,p}(D)}$, where the constant C_{ext} depends only on p, D and U.

Theorem C.3 (Boundary-Trace theorem, c.f. [Alt, 1999], pg. 249, Theorem A 6.6)**.** *Let $D \subset \mathbb{R}^d$ be a bounded, open domain with Lipschitz boundary and $1 \leq p \leq \infty$. There exists a unique linear continuous map*

$$\gamma_0 : W^{1,p}(D) \to L^p(\partial D)$$

such that

(i) $\gamma_0(f) = f|_{\partial D}$ *for all* $f \in W^{1,p}(D) \cap C^0(\overline{D})$,

(ii) $\|\gamma_0(f)\|_{L^p(\partial D)} \leq C_{tr} \|f\|_{W^{1,p}(D)}$, *where the constant* C_{tr} *depends only on* p *and* D.

Theorem C.4 (Characterisation of Trace-zero functions, c.f. [Evans, 1998], pg. 259, Theorem 2)**.** *Let $D \subset \mathbb{R}^d$ be a bounded, open domain with C^1 boundary. Suppose $f \in W^{1,p}(D)$. Then*

$$f \in W_0^{1,p}(D) \text{ if and only if } \gamma_0(f) = 0 \text{ on } \partial D.$$

Theorem C.5 (Compactness of the Boundary-Trace map, c.f. [Alt, 1999], pg. 257, Theorem A 6.13)**.** *Let $D \subset \mathbb{R}^n$ be a bounded, open domain with Lipschitz boundary. Let $1 \leq p < \infty$ and $f_k, f \in W^{1,p}(D)$ for $k \in \mathbb{N}$. Then, as $k \to \infty$,*

$$f_k \rightharpoonup f \text{ in } W^{1,p}(D) \implies \gamma_0(f_k) \to \gamma_0(f) \text{ in } L^p(\partial D).$$

Theorem C.6 (Right inverse of the Boundary-Trace map, c.f. [Grisvard, 2011], pg. 37, Theorem. 1.5.1.2)**.** *Let $k \geq 0$ be an integer and let $D \subset \mathbb{R}^d$ be a bounded, open domain with $C^{k,1}$ boundary. Assume that $s - \frac{1}{p}$ is not an integer, $s \leq k+1, s - \frac{1}{p} > 0$. Then the Boundary-Trace mapping*

$$f \mapsto \gamma_0(f),$$

which is defined for $f \in C^{k,1}(\overline{D})$, has a unique continuous extension as an operator from

$$W^{s,p}(D) \text{ onto } W^{s-\frac{1}{p},p}(\partial D).$$

This operator has a right continuous inverse which does not depend on p.

Theorem C.7 (Right inverse of the conormal Boundary-Trace map, c.f. [Grisvard, 2011], pg. 63, Theorem. 1.6.1.3)**.** *Let $k \geq 0$ be an integer and let $D \subset \mathbb{R}^d$ be*

a bounded, open domain with $C^{k,1}$ boundary ∂D and outward unit normal $\boldsymbol{\nu}$. For $1 \leq i, j \leq d$, let $a_{ij} \in C^\infty(\overline{D})$ and denote $\mathcal{A} = (a_{ij})_{1 \leq i,j \leq d}$. Suppose there exist two constants m, M such that $0 < m \leq M$ and

$$m \leq \left| \sum_{j=1}^{d} a_{ij}(x) \nu_j(x) \right| \leq M \text{ almost everywhere on } \partial D.$$

Then for $s - \frac{1}{p}$ non-integer, $s - \frac{1}{p} > 1$ and $s \leq k+1$, the mapping

$$\begin{aligned} \gamma_{\mathcal{A}} : W^{s,p}(D) &\to W^{s-1-\frac{1}{p},p}(\partial D) \\ f &\mapsto \mathcal{A} \nabla f \cdot \boldsymbol{\nu} \end{aligned}$$

has a right continuous inverse.

Theorem C.8 (Rellich–Kondrachov compactness, c.f. [Alt, 1999], pg. 244, Theorem A 6.4)**.** *Let $D \subset \mathbb{R}^d$ be a bounded, open domain with Lipschitz boundary, $1 \leq p < \infty$ and $m \geq 1$. For $k \in \mathbb{N}$, let $f_k, f \in W^{k,p}(D)$. Then, as $k \to \infty$,*

$$f_k \rightharpoonup f \text{ in } W^{m,p}(D) \implies f_k \to f \text{ in } W^{m-1,p}(D).$$

Theorem C.9 (Co-area formula, c.f. [Evans and Gariepy, 1992], pg. 117, Theorem 2)**.** *Let $\mathcal{L}^k, \mathcal{H}^k$ denote the k-dimensional Lebesgue and Hausdorff measure, respectively. Let $f : \mathbb{R}^n \to \mathbb{R}^m$ with $n \geq m$, $f = (f_1, \ldots, f_m)$. Then for each $\mathcal{L}^n$-summable function $g : \mathbb{R}^n \to \mathbb{R}$,*

$$g|_{f^{-1}\{y\}} \text{ is } \mathcal{H}^{n-m} \text{ summable for } \mathcal{L}^m \text{ almost every } y,$$

and

$$\int_{\mathbb{R}^n} g(x) Jf(x)\, dx = \int_{\mathbb{R}^m} \left[\int_{f^{-1}\{y\}} g \, d\mathcal{H}^{n-m} \right] dy,$$

where $Jf(x) = |\det \nabla f|$ is the Jacobian matrix of f for $\mathcal{L}^n$ almost every x and

$$(\nabla f)_{ij} = \frac{\partial f_i}{\partial x_j} \text{ for } 1 \leq i \leq m, 1 \leq j \leq n.$$

Theorem C.10 (Absolute continuity on lines for $W^{1,p}$ functions, c.f. [Maz'ja, 1985], pg. 8, Theorem 1)**.** *Let $p \geq 1$ and let $D \subset \mathbb{R}^d$ be a bounded, open domain. Then any function in $W^{1,p}(D)$ (possibly modified on a set of measure zero) is absolutely continuous on almost all straight lines which are parallel to the coordinate axes. The*

distributional gradient of a function in $W^{1,p}(D)$ coincides with the usual gradient almost everywhere.

Theorem C.11 (Reflexive weak compactness, c.f. [Evans, 1998], pg. 639, Theorem 3)**.** *Let Y be a reflexive Banach space and suppose the sequence $\{f_k\}_{k=1}^{\infty} \subset Y$ is bounded. Then there exists a subsequence $\{f_{k_j}\}_{j=1}^{\infty} \subset \{f_k\}_{k=1}^{\infty}$ and $f \in Y$ such that*

$$f_{k_j} \rightharpoonup f \text{ as } j \to \infty.$$

Theorem C.12 (Almost everywhere and norm boundedness imply weak convergence, c.f. [Bogachev, 2010], pg. 282, Proposition 4.7.12)**.** *Let $1 < p < \infty$ and let $D \subset \mathbb{R}^d$ be a bounded, open domain. Suppose $f_k \in L^p(D)$ converges almost everywhere (or in measure) to $f \in L^p(D)$. Then, a necessary and sufficient condition for $f_k \rightharpoonup f$ in $L^p(D)$ is the boundedness of $\|f_k\|_{L^p(D)}$.*

Theorem C.13 (Weak convergence and norm convergence imply strong convergence, c.f. [Bogachev, 2010], pg. 285, Corollary 4.7.16)**.** *Let $1 < p < \infty$ and let $D \subset \mathbb{R}^d$ be a bounded, open domain. Suppose $f_k \in L^p(D)$ converges weakly to $f \in L^p(D)$. Assume, in addition, that*

$$\lim_{k\to\infty} \|f_k\|_{L^p(D)} = \|f\|_{L^p(D)}.$$

Then, $\lim_{k\to\infty} \|f_k - f\|_{L^p(D)} = 0$.

Theorem C.14 (Weak lower semicontinuity of the L^p norm, c.f. [Sauvigny, 2012], pg. 172, Theorem 8)**.** *The L^p-norm is lower semicontinuous with respect to weak convergence: Let Y be a Banach space and $1 < p < \infty$. Then*

$$f_k \rightharpoonup f \text{ in } L^p(Y) \implies \|f\|_{L^p(Y)} \leq \liminf_{k\to\infty} \|f_k\|_{L^p(Y)}.$$

Theorem C.15 (Lax–Milgram theorem, c.f. [Evans, 1998], pg. 297, Theorem 1)**.** *Let H be a Hilbert space with norm $\|\cdot\|$ and assume that $B : H \times H \to \mathbb{R}$ is a bilinear mapping, for which there exist constants $\alpha, \beta > 0$ such that*

$$|B[u,v]| \leq \alpha \|u\| \|v\| \text{ and } \beta \|u\|^2 \leq B[u,u] \text{ for all } u, v \in H.$$

Finally, let $f : H \to \mathbb{R}$ be a bounded linear functional on H with duality pairing $\langle \cdot, \cdot \rangle$, then there exists a unique element $u \in H$ such that

$$B[u,v] = \langle f, v \rangle \text{ for all } v \in H.$$

Bibliography

H. Abels. On generalized solutions of two-phase flows for viscous incompressible fluids. *Interfaces and Free Boundaries*, 9:31–65, 2007.

H. Abels. Existence of weak solutions for a diffuse interface model for viscous, incompressible fluids with general densities. *Communications in Mathematical Physics*, 289(1):45–73, 2009a.

H. Abels. On a dffuse interface model for two-phase flows of viscous, incompressible fluids with matched densities. *Archive for Rational Mechanics and Analysis*, 194 (2):463–506, 2009b.

H. Abels. Strong well-posedness of a diffuse interface model for a viscous, quasi-incompressible two-phase flow. *SIAM Journal on Mathematical Analysis*, 44(1): 316–340, 2012.

H. Abels and D. Lengeler. On sharp interface limits for diffuse interface models for two-phase flows. *accepted in Interfaces and Free Boundaries*, 2013.

H. Abels, H. Garcke, and G. Grün. Thermodynamically consistent, frame indifferent diffuse interface models for incompressible two-phase flows with different densities. *Mathematical Models and Methods in Applied Sciences*, 22(3):1150013, 40pp., 2011.

H. Abels, D. Depner, and H. Garcke. On an incompressible Navier–Stokes/Cahn–Hilliard system with degenerate mobility. *Annales de l'Institut Henri Poincare (C) Non Linear Analysis*, 30(6):1175–1190, 2013a.

H. Abels, D. Depner, and H. Garcke. Existence of weak solutions for a diffuse interface model for two-phase flows of incompressible fluids with different densities. *Journal of Mathematical Fluid Mechanics*, 15(3):453–480, 2013b.

F. Aberge and C. Dupaix. Existence of smooth, stationary interfaces for Marangoni-type flow. *Nonlinear Analysis, Theory, Methods and Applications*, 27(11):1329–1350, 1996.

R.A. Adams and J.J.F. Fournier. *Sobolev spaces*. Vol. 140. Academic press, 2003.

M. Alfaro, D. Hilhorst, and H. Matano. The singular limit of the Allen-Cahn equation and the FitzHugh-Nagumo system. *Journal of Differential Equations*, 245 (2):505–565, 2008.

M. Alfaro, H. Garcke, D. Hilhorst, H. Matano, and R. Schätzle. Motion by anisotropic mean curvature as sharp interface limit of an inhomogeneous and anisotropic Allen–Cahn equation. *Proceedings of the Royal Society of Edinburgh: Section A Mathematics*, 140(4):673–706, 2010.

N.D. Alikakos, P.W. Bates, and X. Chen. Convergence of the Cahn–Hilliard equation to the Hele–Shaw model. *Archive for Rational Mechanics and Analysis*, 128(2): 165–205, 1994.

A. Alke and D. Bothe. 3D numerical modeling of soluble surfactant at fluidic interfaces based on the volume-of-fluid method. *FDMP Fluid Dynamics and Material Processes*, 5(4):345–372, 2009.

G. Allain. Small-time existence for the Navier–Stokes equations with a free surface. *Applied Mathematics and Optimization*, 16:37–50, 1987.

H.W. Alt. *Lineare Funktional-analysis*. Springer, 1999.

H.W. Alt. The entropy principle for interfaces. Fluids and solids. *Advances in Mathematical Sciences and Applications*, 19(2):585–663, 2009.

D.M. Anderson, G.B. McFadden, and A.A. Wheeler. Diffuse–interface methods in fluid mechanics. *Annual Review of Fluid Mechanics*, 30(1):139–165, 1998.

L.K. Antanovskii. A phase field model of capillarity. *Physics of Fluids*, 7:747–753, 1995.

R. Aris. *Vectors, Tensors, and the Basic Equations of Fluid Mechanics*. Prentice-Hall, Englewoof Cliffs, NJ, 1962.

J.W. Barrett, R. Nürnberg, and V.M. Styles. Finite element approximation of a phase field model for void electromigration. *SIAM Journal of Numerical Analysis*, 42:738–772, 2004.

J.W. Barrett, H. Garcke, and R. Nürnberg. On the stable numerical approximation of two-phase flow with insoluble surfactant. *Preprint*, 2013.

J.T. Beale. The initial value problem for the Navier–Stokes equation with a free surface. *Communications on Pure and Applied Mathematics*, 34:359–392, 1980.

J.T. Beale. Large-time regularity of viscous surface waves. *Archive for Rational Mechanics and Analysis*, 84:307–352, 1984.

D.N. Bhate, A.F. Bower, and A. Kumar. A phase field model for failure in interconnect lines due to coupled diffusion mechanisms. *Journal of the Mechanics and Physics of Solids*, 50:2057–2083, 2002.

J.F. Blowey and C.M. Elliott. The Cahn–Hilliard gradient theory for phase separation with non-smooth free energy. Part I: Mathematical analysis. *European Journal of Applied Mathematics*, 2(3):233–280, 1991.

J.F. Blowey and C.M. Elliott. Curvature dependent phase boundary motion and parabolic double obstacle problems. In W-M. Ni, L.A. Peletier, and J.L. Vazquez, editors, *Degenerate Diffusions*, pages 19–60. Springer Verlag, New York, 1993.

J.F. Blowey and C.M. Elliott. A phase-eld model with a double obstacle potential. In G. Buttazzo and A. Visintin, editors, *Motion by Mean Curvature and Related Topics: Proceedings of the International Conference held at Trento, Italy, July 20-24, 1992*, pages 1–22. de Gruyter, 1994.

V.I. Bogachev. *Differentiable measures and the Malliavin calculus.* Mathematical Surveys and Monographs, Volume 164, American Mathematical Society, Providence, RI, 2010.

D. Bothe and J. Prüss. Stability of equilibria for two-phase flows with soluble surfactant. *The Quarterly Journal of Mechanics and Applied Mathematics*, 63(2), 2010.

D. Bothe, J. Prüss, and G. Simonett. Well-posedness of a two-phase flow with soluble surfactant. In H. Brezis, M. Chipot, and J. Escher, editors, *Nonlinear Elliptic and Parabolic problems, Progress in Nonlinear Differential Equations and Their Applications*, volume 64, pages 37–61. Springer, New York, 2005.

F. Boyer. Mathematical study of multi-phase flow under shear through order parameter formulation. *Asymptotic Analysis*, 20(2):175–212, 1999.

F. Boyer. Nonhomogeneous Cahn–Hilliard fluids. *Annales de l'Institut Henri Poincare (C) Non Linear Analysis*, 18(2):225–259, 2001.

K.A. Brakke. *The motion of a surface by its mean curvature.* Mathematical Notes, Princeton University Press, 1978.

L. Bronsard and R.V. Kohn. Motion by mean curvature as the singular limit of Ginzburg–Landau dynamics. *Journal of Differential Equations*, 90:211–237, 1991.

B.P. Brooks. The coefficients of the characteristic polynomial in terms of the eigenvalues and the elements of an $n \times n$ matrix. *Applied mathematics letters*, 19(6): 511–515, 2006.

G. Caginalp. Stefan and Hele–Shaw type models as asymptotic limits of the phase field equations. *Physical Review A*, 39:5887–5896, 1989.

G. Caginalp and X. Chen. Convergence of the phase field model to its sharp interface limits. *European Journal of Applied Mathematics*, 9(4):417–445, 1998.

J.W. Cahn, C.M. Elliott, and A. Novick-Cohen. The Cahn–Hilliard equation with a concentration dependent mobility: motion by minus the Laplacian of the mean curvature. *European Journal of Applied Mathematics*, 7(3):287–302, 1996.

E.A. Carlen, M.C. Carvalho, and E. Orlandi. Approximate solutions of the Cahn–Hilliard equation via corrections to the Mullins–Sekerka motion. *Archive for Rational Mechanics and Analysis*, 178(1):1–55, 2005.

P. Cermelli, E. Fried, and M.E. Gurtin. Transport relations for surface intgerals arising in the formulation of balance laws for evolving fluid interfaces. *Journal of Fluid Mechanics*, 544:339–351, 2005.

Y.C. Chang, T.Y. Hou, B. Merriman, and S. Osher. A level set formulation of Euleran interface caputring methods for incompressible fluid flows. *Journal of Computational Physics*, 124:449–464, 1996.

X. Chen. Generation and propagation of interfaces in reaction-diffusion systems. *Transactions of the American Mathematical Society*, 334(2):877–913, 1992a.

X. Chen. Generation and propagation of interfaces in reaction-diffusion equations. *Journal of Differential Equations*, 96(1):116–141, 1992b.

X. Chen. Spectrum for the Allen–Cahn, Cahn–Hillard, and phase-field equations for generic interfaces. *Communications in Partial Differential Equations*, 19(7–8): 1371–1395, 1994.

X. Chen. Global asymptotic limit of solutions of the Cahn–Hilliard equation. *Journal of Differential Geometry*, 44:262–311, 1996.

X. Chen and C.M. Elliott. Asymptotics for a parabolic double obstacle problem. *Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences*, 444(1992):429–445, 1994.

F.A. Coutelieris. The effect of geometry and axial orientation of spheroidal particles on the adsorption rate in a granular porous medium. *Studies in Surface Science and Catalysis*, 144:745–751, 2002.

F.A. Coutelieris, M.E. Kainourgiakis, and A.K. Stubos. Low Peclet mass transport in assemblages of spherical particles for two different adsorption mechanisms. *Journal of Colloid and Interface Science*, 264:20–29, 2003.

F.A. Coutelieris, M.E. Kainourgiakis, and A.K. Stubos. Low to moderate Peclet mass transport in assemblages of spherical particles for a realistic adsorption-reaction-desorption mechanism. *Powder Technology*, 159:173–179, 2005.

P. De Mottoni and M. Schatzman. Geometrical evolution of developed interfaces. *Transactions of the American Mathematical Society*, 347(5):1533–1589, 1995.

I.V. Denisova. Evolution of compressible and incompressible fluids separated by a closed interface. *Interfaces and Free Boundaries*, 2:283–312, 2000.

H. Diamant and D. Andelman. Kinetics of surfactant adsorption at fluid–fluid interfaces. *Journal of Physical Chemistry*, 100:13732–13742, 1996.

H. Diamant, G. Ariel, and D. Andelman. Kinetics of surfactant adsorption: the free energy approach. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 183:259–276, 2001.

H. Ding, P.D.M. Spelt, and C. Shu. Diffuse interface model for incompressible two-phase flows with large density ratios. *Journal of Computational Physics*, 226(1): 2078–2095, 2007.

G. Dziuk and C.M. Elliott. Finite element methods for surface PDEs. *Acta Numerica*, 22:289–396, 2013.

J. Eastoe and J.S. Dalton. Dynamic surface tension and adsorption mechanisms of surfactants at the air–water interface. *Advances in Colloid and Interface Science*, 85:103–144, 2000.

C.M. Elliott and R. Schätzle. The limit of the fully anisotropic double-obstacle Allen–Cahn equation in the nonsmooth case. *SIAM Journal of Mathematical Analysis*, 28(2):274–303, 1997.

C.M. Elliott and B. Stinner. Analysis of a diffuse interface approach to an advection diffusion equation on a moving surface. *Mathematical Models and Methods in Applied Sciences*, 19(5):787–802, 2009.

C.M. Elliott, B. Stinner, V. Styles, and R. Welford. Numerical computation of advection and diffusion on evolving diffuse interfaces. *IMA Journal of Numerical Analysis*, 31(3):786–812, 2011.

S. Engbolm, M. Do-Quang, G. Amberg, and A-K. Tornberg. On modeling and simulation of surfactants in diffuse interface flow. *Communications in Computational Physics*, 14(4):875–915, 2013.

L.C. Evans. *Partial differential equations.* American Mathematical Society, 1998.

L.C. Evans and R.F. Gariepy. *Measure theory and the fine properties of functions.* Studies in Advanced Mathematics, CRC Press, 1992.

L.C. Evans, H.M. Soner, and P.E. Souganidis. Phase transitions and generalized motion by mean curvature. *Communications on Pure and Applied Mathematics*, 45(9):1097–1123, 1992.

X. Feng. Fully discrete finite element approximations of the Navier–Stokes–Cahn–Hilliard diffuse interface model for two-phase fluid flows. *SIAM Journal on Numerical Analysis*, 44(3):1049–1072, 2006.

X. Feng and A. Probl. Numerical analysis of the Allen–Cahn equation and approximation for mean curvature flows. *Numerische Mathematik*, 94:33–65, 2003.

X. Feng and A. Probl. Analysis of a fully discrete finite element method for the phase field model and approximation of its sharp interface limits. *Mathematics of Computation*, 73(246):541–567, 2004.

X. Feng and A. Probl. Numerical analysis of the Cahn–Hilliard equation and approximation for the Hele–Shaw problem. *Interfaces and Free Boundaries*, 7:1–28, 2005.

X. Feng, Y. He, and C. Liu. Analysis of finite element approximations of a phase field model for two-phase fluids. *Mathematics of Computation*, 76(258):539–571, 2007.

J. Fernandez and G.M. Homsy. Chemical reaction-driven tip-streaming phenomena in a pendant drop. *Physics of Fluids*, 16:2548–2555, 2004.

P.C. Fife and O. Penrose. Interfacial dynamics for thermodynamically consistent phase-field models with nonconserved order parameter. *Electronic Journal of Differential Equations*, 1995(16):1–49, 1995.

S. Franz, R. Gärtner, H-G. Roos, and A. Voigt. A note on the convergence analysis of a diffuse domain approach. *Computational Methods in Applied Mathematics*, 12(2):153–167, 2012.

E. Fried and M.E. Gurtin. Continuum theory of thermally induced phase transitions based on an order parameter. *Physica D: Nonlinear Phenomena*, 68:326–343, 1993.

S. Ganesan and L. Tobiska. A coupled arbitrary Lagrangian–Eulerian and Lagrangian method for computation of free surface flows with insoluble surfactants. *Journal of Computational Physics*, 228(8):2859–2873, 2009.

H. Garcke and D.J.C. Kwak. On asymptotic limits of Cahn–Hilliard systems with elastic misfit. In *Analysis, modeling and simulation of multiscale problems*, pages 87–111. Springer Berlin Heidelberg, 2006.

H. Garcke and B. Stinner. Second order phase field asymptotics for multi-component systems. *Interfaces and Free Boundaries*, 8:131–157, 2006.

H. Garcke, K.F. Lam, and B. Stinner. Diffuse interface modelling of soluble surfactants in two-phase flow. *Communications in Mathematical Science*, 12(8):1475–1522, 2014.

Y. Giga and S. Takahasi. On global weak solutions of the nonstationary two-phase stokes flow. *SIAM Journal of Mathematical Analysis*, 25(3):876–893, 1994.

D. Gilbarg and N. Trudinger. *Elliptic partial differential equations of second order*. Springer, Berlin, 1983.

P. Grisvard. *Elliptic problems in nonsmooth domains*. Vol. 69 Society for Industrial and Applied Mathematics, 2011.

S. Gross and A. Reusken. *Numerical Methods for two-phase incompressible flows*. Springer-Verlag, Berlin, 2011.

G. Grün. On convergent schemes for diffuse interface models for two-phase flow of incompressible fluids with general mass densities. *SIAM Journal of Numerical Analysis*, 51(6):3036–3061, 2013.

M.E. Gurtin, D. Polignone, and J. Viñals. Two-phase binary fluids and immiscible fluids described by an order parameter. *Mathematical Models and Methods in Applied Sciences*, 6(6):815–831, 1996.

P.C. Hohenberg and B.I. Halperin. Theory of dynamic critical phenomena. *Reviews of Modern Physics*, 49(3):435–479, 1977.

T. Ilmanen. Convergence of the the Allen–Cahn equation to Brakke's motion by mean curvature. *Journal of Differential Geometry*, 38(2):417–461, 1993.

A.J. James and J. Lowengrub. A surfactant-conserving volume-of-fluid method for interfacial flows with insoluble surfactant. *Journal of Computational Physics*, 201: 685–722, 2004.

D. Kay, V.M. Styles, and R. Welford. Finite element approximation of a Cahn-Hilliard-Navier-Stokes system. *Interfaces and Free Boundaries*, 10:15–43, 2008.

S. Khatri and A-K. Tornberg. A numerical method for two phase flows with insoluble surfactants. *Computers and Fluids*, 49:150–165, 2011.

J. Kim. A continuous surface tension force formulation for diffuse-interface models. *Journal of Computational Physics*, 204:784–804, 2005.

P.A. Kralchevsky, K.D. Danov, G. Broze, and A. Mehreteab. Thermodynamics of ionic surfactant adsorption with account for the counterion binding: effect of salts of various valency. *Langmuir*, 15:2351–2365, 1999.

P.A. Kralchevsky, K.D. Danov, and N.D. Denkov. Chemical physics of colloid systems and interfaces. In K. S. Birdi, editor, *Chapter 7 in Handbook of Surface and Colloid Chemistry*, pages 199–355. CRC Press, Boca Raton, 2008.

R. Krechetnikov and G.M. Homsy. On physical mechanisms in chemical reaction-driven tip-streaming. *Physics of Fluids*, 16:2556–2566, 2004a.

R. Krechetnikov and G.M. Homsy. On a new surfactant-driven fingering phenomenon in a Hele-Shaw cell. *Journal of Fluids Mechanics*, 509:103–124, 2004b.

A. Kufner and B. Opic. How to define reasonably weighted Sobolev spaces. *Commentationes Mathematicae Universitatis Carolinae*, 25(3):537–554, 1984.

M.L. Lagunova. On the solvability of a three-dimensional problem of thermocapillary convection. *Journal of Soviet Mathematics*, 64(6):1233–1240, 1993.

M-C. Lai, Y-H. Tseng, and H. Huang. An immersed boundary method for interfacial flows with insoluble surfactant. *Journal of Computational Physics*, 227:7279–7293, 2008.

H.G. Lee and K. Junseok. Regularized Dirac delta functions for phase field models. *International Journal for Numerical Methods in Engineering*, 91(3):269–288, 2012.

X. Li, J. Lowengrub, A. Rätz, and A. Voigt. Solving PDEs in complex geometries: a diffuse domain approach. *Communications in Mathematical Sciences*, 7(1):81–107, 2009.

X. Li, R. Shaw, G.M. Evans, and P. Steveson. A simple numerical solution to the Ward–Tordai equation for the adsorption of non–ionic surfactants. *Computers and Chemical Engineering*, 34:146–153, 2010.

Y. Li and J. Kim. A comparison study of phase-field models for an immiscible binary mixture with surfactant. *The European Physical Journal B-Condensed Matter and Complex Systems*, 85(10):1–9, 2012.

C. Liu and J. Shen. A phase field model for the mixture of two incompressible fluids and its approximation by a Fourier-spectral method. *Physica D*, 179:211–228, 2003.

C. Liu, J. Shen, J.J. Feng, and P. Yue. Variational approach in two-phase flows of complex fluids: transport and induced elastic stress. *Mathematical Models and Methods in Phase Transitions,. Nova Publications*, 2005.

H. Liu and Y. Zhang. Phase-field modeling droplet dynamics with soluble surfactants. *Journal of Computational Physics*, 229:9166–9187, 2010.

J. Lowengrub and L. Truskinovsky. Quasi-incompressible Cahn–Hilliard fluids and topological transitions. *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, 454:2617–2654, 1998.

J. Lowengrub, J. Goodman, H. Lee, E.K. Longmire, M. Shelley, and L. Truskinovsky. Topological transitions in liquid/liquid interfaces. *Chapman & Hall/CRC Res. Notes Math 409 (Free Boundary Problems: Theory and Applications, Crete 1997)*, 409:221–236, 1999.

E. Marušić-Paloka. Two methods for replacing Dirichlet's boundary condition by Robin's boundary condition via penalization. *Mathematical Communications*, 4: 27–33, 1999.

MATLAB. *Version 7.11.0 (R2010b)*. The MathsWorks Inc., Natick, Massachusetts, 2010.

V.G. Maz'ja. *Sobolev spaces*. Springer–Verlag, Berlin–Heidelberg–New York, 1985.

V.G. Maz'ja and S.V. Poborchi. *Differentiable functions on bad domains*. World Scientific, 1997.

B. Merriman and S.J. Ruuth. Diffusion generated motion of curves on surfaces. *Journal of Computational Physics*, 225(2):2267–2282, 2007.

L. Modica and S. Mortola. Un esempio di Gamma-convergenza. *Boll. Un. Mat. Ital. B*, 14(5):285–299, 1977.

M. Muradoglu and G. Tryggvason. A front-tracking method for computation of interfacial flows with soluble surfactants. *Journal of Computational Physics*, 227: 2238–2262, 2008.

R.H. Nochetto and C. Verdi. Convergence of double obstacle problems to the geometric motions of fronts. *SIAM Journal of Mathematical Analysis*, 26(6):1514–1526, 1995.

R.H. Nochetto, M. Paolini, and C. Verdi. Sharp error analysis for curvature dependent evolving fronts. *Mathematical Models and Methods in Applied Sciences*, 3: 711–723, 1993.

A. Nouri and F. Poupaud. An existence theorem for the multifluid Navier–Stokes problem. *Journal of Differential Equations*, 122:71–88, 1995.

J. Prüss and G. Simonett. On the two-phase Navier–Stokes equations with surface tension. *Interfaces and Free Boundaries*, 10:311–345, 2010.

A. Rätz and A. Voigt. PDE's on surfaces—a diffuse interface approach. *Communications in Mathematical Sciences*, 4(3):575–590, 2006.

Y.Y. Renardy, M. Renardy, and V. Cristini. A new volume-of-fluid formulation for surfactants and simulations of drop deformation under shear at a low viscosity ratio. *European Journal of Mechanics-B/Fluids*, 21(1):49–59, 2002.

M. Röger and Y. Tonegawa. Convergence of phase-field approximations to the Gibbs-Thomson law. *Calculus of Variations and Partial Differential Equations*, 32(1):111–136, 2008.

F. Sauvigny. *Partial Differential Equations 1: Foundations and Integral Representations*. Springer–Verlag, Berlin–Heidelberg–New York, 2012.

A. Schmidt and K.G. Siebert. *Design of adaptive finite element software: The finite element toolbox ALBERTA*. Springer Verlag, 2005.

L.E. Scriven. Dynamics of a fluid interface equation of motion for Newtonian surface fluids. *Chemical Engineering Science*, 12(2):98–108, 1960.

D Silvester, H. Elman, D. Kay, and A. Wathen. Efficient preconditioning of the linearized Navier–Stokes equations for incompressible flow. *Journal of Computational and Applied Mathematics*, 128:261–279, 2001.

V.A. Solonnikov. Solvability of a problem on the motion of a viscous incompressible fluid bounded by a free surface. *Mathematics of the USSR-Izvestiya*, 11(6):1323–1358, 1977.

V.A. Solonnikov. Solvability of the problem of evolution of an isolated volume of viscous incompressible capillary fluid. *Journal of Soviet Mathematics*, 32(2):223–228, 1986.

H.M. Soner. Convergence of the phase-field equations to the Mullins–Sekerka problem wih kinetic undercooling. *Archive for Rational Mechanics and Analysis*, 131 (2):139–197, 1995.

H.A. Stone. A simple derivation of the time-dependent convective-diffusion equation for surfactant transport along a deforming interface. *Physics of Fluids A: Fluid Dynamics*, 2:111, 1990.

B.E.E. Stoth. Convergence of the Cahn–Hilliard equation to the Mullins–Sekerka problem in spherical symmetry. *Journal of Differential Equations*, 125(1):154–183, 1996.

P. Sun, C. Liu, and J. Xu. Phase field model of thermo-induced Marangoni effects in the mixtures and its numerical simulations with mixed finite element method. *Communications in Computational Physics*, 6(5):1095–1117, 2009.

M. Sussman, P. Smerka, and S. Osher. A level set approach for computing solutions to incompressible two-phase flow. *Journal of Computational Physics*, 114:146–159, 1994.

N. Tanaka. Global existence of two phase nonhomogeneous viscous incompressible fluid flow. *Communications in Partial Differential Equations*, 18(1-2):41–81, 1993.

N. Tanaka. Two-phase free boundary problem for viscous incompressible thermo-capillary convection. *Japanese Journal of Mathematics. New Series*, 21(1):1–42, 1995.

A. Tani. Small-time existence for the three-dimensional Navier–Stokes equations for an incompressible fluid with a free surface. *Archive for Rational Mechanics and Analysis*, 133:299–331, 1996.

A. Tani and N. Tanaka. Large-time existence of surface waves in incompressible viscous fluids with or without surface tension. *Archive for Rational Mechanics and Analysis*, 130:303–314, 1995.

K.E. Teigen, X. Li, J. Lowengrub, F. Wang, and A. Voigt. A diffuse-interface approach for modeling transport, diffusion and adsorption/desorption of material quantities on a deformable interface. *Communications in Mathematical Sciences*, 7(4):1009–1037, 2009.

K.E. Teigen, P. Song, J. Lowengrub, and A. Voigt. A diffuse-interface method for two-phase flows with soluble surfactants. *Journal of Computational Physics*, 230: 375–393, 2011.

T. Teramoto and F. Yonezawa. Droplet growth dynamics in a water/oil/surfactant system. *Journal of Colloid and Interface Science*, 235(2):329–333, 2001.

O. Theissen and G. Gompper. Lattice-Boltzmann study of spontaneous emulsification. *The European Physical Journal B-Condensed Matter and Complex Systems*, 11(1):91–100, 1999.

S.O. Unverdi and G. Tryggvason. A front-tracking method for viscous, incompressible, multi-fluid flows. *Journal of Computational Physics*, 100(1):25–37, 1992.

R.G.M. van der Sman and S. van der Graaf. Diffuse interface model of surfactant adsorption onto flat and droplet interfaces. *Rheology Acta*, 46:3–11, 2006.

A. Wagner. Nonstationary marangoni convection. *Applicationes Mathematicae*, 26 (2):195–220, 1999.

A.F.H. Ward and L. Tordai. Time dependence of boundary tensions of solutions I. The role of diffusion in time effects. *Journal of Chemical Physics*, 14(7):453–461, 1946.

H. Wong, D. Rumschitzki, and C. Maldarelli. On the surfactant mass balance at a deforming fluid interface. *Physics of Fluids*, 8:3203–3204, 1996.

J-J. Xu, Y. Huang, M-C. Lai, and Z. Li. A coupled immersed interface and level set method for three-dimensional interfacial flows with insoluble surfactant. *Communications in Computational Physics*, 15(2):451–469, 2014.

J.J. Xu, Z. Li, J. Lowengrub, and H. Zhao. A level-set method for interfacial flows with surfactant. *Journal of Computational Physics*, 212(2):590–616, 2006.

L. Xu and Z. Zhang. On the free boundary problem to the two viscous immiscible fluids. *Journal of Differential Equations*, 248:1044–1111, 2010.

X. Yang and A.J. James. An arbitrary Langrangian–Eulerian (ALE) method for interfacial flows with insoluble surfactants. *FDMP Fluid Dynamics and Material Processes*, 3(1):65–95, 2009.

S. Yon and C. Pozrikidis. A finite-volume/boundary-element method for flow past interfaces in the presence of surfactants, with application to shear flow past a viscous drop. *Computations & Fluids*, 27(8):879–902, 1998.

V.P. Zhdanov. Adsorption-desorption kinetics and chemical potential of adsorbed and gas-phase particles. *Journal of Chemical Physics*, 114(10):4746–4748, 2001.